Handbook of Environmental Analysis

Third Edition

Chemical Pollutants in Air, Water, Soil, and Solid Wastes

Pradyot Patnaik

CRC Press
Taylor & Francis Group

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To

Sanjukta, Manisha, Megha, and Chirag

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SECTION II Specific Classes of Substances and Aggregate Properties

Preface

The field of environmental analysis has continued to expand over the years in parallel to the large-scale uses of many new classes of chemicals for their industrial, pharmaceutical, agricultural, and household applications. Many such substances released into the environment after their end use and also a number of their breakdown products are prone to contaminate the air, aquatic environment, and soils and sediments. New analytical methods for their detection and quantification at trace levels are being developed for several such emerging contaminants. While the general analytical tools for measuring most pollutants in the environmental matrices may be the same as that used for macro chemical analyses, the extraction techniques, the quality control measures, and also the methods of quantifying such substances may vary, however, for the environmental analyses of terrace pollutants.

Five new chapters have been incorporated into this third edition. The topics are Derivatization Reactions in Trace Chemical Analysis; Emerging Pollutants: Classification, Extractions, and Analytical Techniques—An Overview; Emerging Pollutants: Nanomaterials; Chlorine and Chloramines; and Microbial Analysis. The inclusion of a chapter on microbial analysis in this edition though extending outside the domains of chemical analysis, should however fall within the broader and general concepts of environmental analysis. Section III section highlighting selected individual compounds has been retained in this edition, although their methods of analysis may be found in Section II under specific classes of compounds. Also, the appendices listing method numbers for substances have been retained which are partial lists only and not the full lists, to keep this book within reasonable size. Greater emphasis, however, is focused in this book on the analytical reactions pertaining to the chemical structures and the functional groups in compounds to enable readers to come up with an analytical procedure for a substance for which there is no analytical method available.

Any thoughts, comments, or suggestions from the readers on any error or omission or for the improvement of the contents of this book are most humbly solicited.

Pradyot Patnaik
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Dr. Patnaik earned his BS (Honors) and MS in chemistry from Utkal University, India and PhD from the Indian Institute of Technology, Bombay, India. After that he worked at Hindustan Lever Research Center at Bombay and then as a postdoctoral research scientist at Cornell University, Ithaca, New York.

Dr. Patnaik has authored three other books: *A Comprehensive Guide to the Hazardous Properties of Chemical Substances* (John Wiley, New York), the *Handbook of Inorganic Chemicals* (McGraw-Hill, New York), and *Dean's Analytical Chemistry Handbook* (McGraw-Hill, New York).

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Section I

Analytical Techniques

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1 Environmental Analysis: An Overview

The field of environmental analysis has grown rapidly in recent years, thus becoming an important area of analytical science involving innovative developments of new analytical techniques to identify and quantify trace pollutants in the environment. The fast growth of this branch of science may be attributed not only to the large number of pollutants that are being continually released into the environment from many industrial processes and generation of synthetic products but also to their physical and chemical properties. The wide array of such substances among others includes many disinfection by-products, pharmaceuticals, household wastes, agricultural chemicals, and nanomaterials. Also, the society's concern on the impact from the chronic exposures to such substances on humans, animals, aquatic species, vegetations, and also any possible climatic change, as well as promulgations of more stringent requirements from the regulatory agencies on monitoring concentrations of such substances at trace levels with high precisions and accuracy at statistically defined confidence levels to achieve high data quality, have catapulted this field over the past two or three decades from its dawn to a distinctive era. This has also entailed, along with modifications in instrumentations, sampling procedures and the sample preparation techniques to achieve such low levels of detections at a faster speed of analysis.

It may be noted here that like any other scientific field environmental analysis relies heavily on instrumentation and in this regard its approach essentially has remained the same as to the conventional macro, and semi-micro chemical analysis. Organic pollutants are primarily determined by gas chromatography (GC), GC/mass spectrometry (MS), and high-performance liquid chromatography (HPLC), methods. These techniques, however, are not adequate to measure several classes of the so-called emerging pollutants. The field of MS, therefore, has broadened from the low-resolution to the high-resolution stage and from the electron-impact to the electrospray ionization mode in order to detect and quantify pollutants at much lower concentrations. New methods involving liquid chromatography (LC)/MS are being developed to measure pollutants of larger molecular masses that cannot be determined by GC/MS. However, there is also a growing interest in alternative techniques, such as Fourier transform infrared spectroscopy (FTIR). Specially designed capillary columns have come up for GC analysis to achieve high resolution and better separation of many closely eluting isomers. Another major development in organic analysis is HPLC determination using postcolumn derivatization. Many classes of substances such as aldehydes, ketones, and carboxylic acids may be accurately determined by using such techniques.

The mass spectrometry techniques (GC/MS or LC/MS) should be used wherever possible to identify organic compounds in the sample. Although it has a lower sensitivity than other GC detectors, mass spectrometry is by far the most confirmative test for compound identification. Like all analytical techniques, it has limitations too, such as its inability to distinguish between the isomers of a compound. Also, it may be noted here that the analysts must use their judgment and understanding of chemical structures to identify compounds before reporting their presence in the sample, rather than strictly adhering to the mass spectral library search results even with the best matches. This, sadly, has become the common trend today, which may contribute to false identification of a compound that may not be present in the sample. It is therefore always advisable to use combinations of multiple techniques to confirm the presence of toxic pollutants if detected, and also use the internal standard calibration methods in quantifying.

One of the key steps in all environmental analyses involves sample preparation. Be it an aqueous or a solid matrix, for organic analyses the pollutants usually need to be extracted into an appropriate solvent with greater solubility and also immiscible in water. This should be followed by a clean-up of the solvent extracts prior to their analyses. Several methods are commonly employed, such as the "purge and trap" concentration for volatile organic compounds, the liquid-liquid- and

solid-phase extractions for aqueous samples, and the thermal desorption, sonication, and supercritical fluid extractions for solid samples. There has been a spurt of research in the areas of solid-phase extractions and the supercritical fluid extractions, although these methods are known for long. Both techniques have made the extraction of pollutants from aqueous and nonaqueous matrices relatively simple, fast, and less expensive. These processes, along with gel permeable chromatography, provide efficient methods for removing interferences. An interesting area of noteworthy research is the micro-extraction using multiwalled carbon nanotubes, which apparently seems to be years away from making any inroad into the routine extraction procedures for aqueous samples.

Methodologies for inorganic anions and metals have undergone rapid growth similar to chromatographic techniques. Notable among these technologies are atomic absorption and emission spectroscopy and ion chromatography (IC). The latter is a rapid method to determine several anions, simultaneously. The IC approach may be modified further to measure such weak anions as carboxylates and cyanide.

The analytical methods of measuring pollutants in ambient air have developed tremendously in recent years. Although these methods employ the same analytical instrumentation (i.e., GC, GC/MS, HPLC, IR, atomic absorption, IC, and the electrode methods), the air sampling technique is probably the most important component of such analysis. The use of cryogenic traps and high-pressure pumps has supplemented the impinger and sorbent tube sampling techniques. The sorbent tubes are used commonly for sampling indoor air to measure a wide array of organic compounds.

The pollutants that are currently regulated constitute only a fraction of those found in the environment. In addition, their chemical characteristics and concentrations may vary widely. New and alternative methodologies that are simple, rapid, and reliable need to be developed. Enzyme immunoassay and portable GC and IR techniques need greater attention. Another area of interest, with future applications, is the application of functionalized carbon nanotubes for specific analyses. In the separation field, micromembrane techniques appear promising for the future.

Atomic absorption and emission spectroscopy have continued to remain as the exclusive analytical techniques to measure trace metals in environmental samples. Although the metals can be analyzed by various other methods, atomic spectroscopy offers the lowest desired detection levels and is also cheaper and faster in comparison to most other instrumental methods, such as the neutron activation analysis and x-ray methods. Among the wet methods, colorimetric analysis using a spectrophotometer or a filter photometer, though susceptible to interferences, still constitutes over measuring 50% of all wet parameters. The ion-selective electrode methods, though, have limited applications and are still useful for measuring many anions and neutral molecules at desired low levels of detections. In comparison, the classical titrimetric procedures that can be applied to determine many substances in waters have, however, found only some degree of applications in environmental analyses.

The fast growth of technology in recent years has placed too much emphasis on new instrumentations, mostly toward their development and upgrading. Although that has helped the efficacy and speed of many tedious analyses, there, however, has been a lack of implementation of or any serious interest among the environmental analytical community toward many novel derivatization reactions that are being reported in the analytical research journals. Such reactions applied to analyze trace organic pollutants should be able to improve the screening process to confirm the presence of pollutants, and also enhance their quantifications. The instrumental analyses should therefore move along in conjugation with chemistry.

Readers may find an in-depth discussion on all aspects of environmental trace analyses in this book, including instrumentations, as well as sample preparation techniques and analytical procedures and their chemical reactions. The substances are grouped under various broad headings in accordance with their physicochemical nature, industrial applications, or their functional groups in the molecules. Many derivatization reactions are highlighted all throughout. Also, the emerging pollutants of interest and statistics in trace analyses are discussed in detail. The individual compounds and the appendices from the previous edition and the radionuclides analyses are retained in this edition. The biochemical analyses of coliform bacteria that are foremost criteria to determine the water quality are incorporated into this edition, which is an important feature of this book.

2 Precision and Accuracy of Analysis

STATISTICS IN ENVIRONMENTAL ANALYSIS

Statistics is applied broadly in all areas of sciences for a variety of purposes, such as to build models with existing data in order to estimate parameters, select among alternate models, test hypotheses, and make predictions. Its scope generally is broad and interferences are usually determined from comparative measurements. In environmental sciences, its applications also vary. For example, studies related to climatic change often use statistical models to test hypotheses. On the other hand, for field samplings, statistical concepts may be applied to design a specific sampling scheme based on the collected data on the samples, and also the sample "populations," defined as collection of all the possible observations of interest. However, it may be noted here that any overuse of statistical methods for environmental data analysis may draw very different conclusions if the pitfalls are not identified. There are four statistical methods commonly used in environmental data analysis. The most common of these is the estimation of percentile and confidence interval. It is, however, based on the automatic assumption of a normal distribution to environmental data. However, for heavily contaminated samples, such normal distribution is susceptible to be skewed. The other statistical methods of use are correlation coefficient, regression analysis, and analysis of variance. In the correlation coefficient method, a wide range of data points are used where the data points with maximum values may trivialize other small data points and may consequently skew the correlation coefficient. Similarly, the other two methods which are applied in modeling may have drawbacks too. The regression analysis may give a model which may be more uncertain if the input variables propagate uncertainties. The weakness in the analysis of variance method may be attributed to the acceptance of hypothesis as a weak argument to imply a strong conclusion. The pitfalls of all these methods should be understood and identified. They, however, should not come into play in reference to the trace analyses of pollutants or parameters.

In environmental analysis, the percentile and confidence intervals are often taken into consideration in the measurements. There are three major areas in environmental where statistical concepts are applied. One is in the determination of precision or reproducibility of measurements. Even for measuring the precision in routine analysis, relative percent difference (RPD) are used in the duplicate analyses to determine the precision rather measuring the relative standard deviation or the coefficient of variance of multiple analyses. However, the standard deviations in the measurements are determined to construct the precision control charts as well as the accuracy control charts. The control charts thus use the normal distribution statistics. The other area of applications of statistical concepts is in the determination of method detection limits (MDL), mostly for the chromatography analyses of organic pollutants. The statistics involved here is t-statistics for a lesser number of sample aliquots where the standard deviations of measurements are multiplied by the t-values for the corresponding degrees of freedom. Some of these statistical concepts and their applications have been specified or defined under the procedures approved by the regulatory agencies. They form part of the quality control and quality assurance programs highlighted below. The precision and accuracy of measurements are discussed in the following sections with examples of problems and calculations.

Another area of environmental analyses where one may see the use of statistics is in the microbial analyses for the determination of coliform bacteria by the most probable number (MPN) method

involving multiple tube fermentation techniques. This method is commonly used in routine microbiological analyses along with, different though however, from the other method, the membrane filter test in which the coliform colonies are counted. The methods are discussed in detail in this book under Microbial Analysis, Chapter 15.

QUALITY ASSURANCE AND QUALITY CONTROL IN ENVIRONMENTAL ANALYSIS

Quality assurance and quality control programs mandate that every laboratory follow a set of well-defined guidelines so as to achieve analytical results with a high degree of accuracy. The term quality assurance refers to a set of principles that are defined, documented, and strictly observed such that the accuracy of the results of analysis may be stated with a high level of confidence and is legally defensible. The quality assurance plan includes documentation of sampling events, receipt of samples in the laboratory, and relinquishment of samples to respective individuals who perform the analysis. All these events are recorded on chain-of-custody forms with dates and times, as well as the names and signatures of the individuals who are responsible for performing the tasks. The plan, in a broader sense of the term, also includes quality control.

The laboratory quality control program has several components: the documentation of standard operating procedures for all analytical methods, the periodic determination of method detection levels for the analytes, the preparation of standard calibration curves and the daily check of calibration standards, the analysis of reagent blank, the checking of instrument performance, the determination of precision and accuracy of analysis, and the preparation of control charts. The determination of precision and the accuracy of analysis and method detection limits are described under separate subheadings in the following sections. The other components of the quality control plan are briefly discussed below.

The preparation of a standard calibration curve is required for many colorimetric and gas chromatography analyses. A fresh calibration check standard at any selected concentration should be prepared daily and analyzed prior to sample analysis. If the response for the check standard falls outside of $\pm 15\%$ standard deviation for the same concentration in the standard calibration curve, then a new calibration curve should be prepared.

PRECISION AND ACCURACY

The determination of precision and accuracy is an important part of environmental analysis because it indicates the degree of bias or any error in the measurement.

Precision determines the reproducibility or repeatability of the analytical data. It measures how closely multiple analyses of a given sample agree with each other. If a sample is repeatedly analyzed under identical conditions, the results of each measurement, x, may vary from each other due to experimental error or causes beyond control. These results will be distributed randomly about a mean value that is the arithmetic average of all measurements. If the frequency is plotted against the results of each measurement, a bell-shaped curve known as normal distribution curve or Gaussian curve will be obtained, as shown in Figure 2.1. (In many highly dirty environmental samples, the results of multiple analyses may show skewed distribution and not normal distribution.)

The mean x of all distributions is equal to $\sum x/n$ (i.e., the sum of all measurements divided by the number of measurements). Standard deviation, which fixes the width of the normal distribution, consists of a fixed fraction of the values making up the curve. An estimate of standard deviation, s, can be calculated as follows:

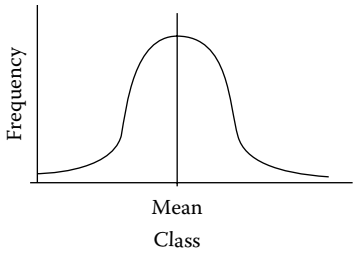

FIGURE 2.1 Normal distribution curve.

$$s = \sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}}$$

In a normal distribution curve, 68.27% of area lies between $x \pm 1s$, 95.45% of area lies between $x \pm 2s$, and 99.70% of area falls between $x \pm 3s$. In other words, 99.70% of replicate measurement should give values that should theoretically fall within three standard deviations about the arithmetic average of all measurements. Therefore, $3s$ about the mean is taken as the upper and lower control limits (UCL and LCL) in control charts. Any value outside $x \pm 3s$ should be considered unusual, and indicates some problem in the analysis that must be addressed immediately.

Standard deviation can be calculated alternatively from the following equation, which does not differ much from the one shown above:

$$s = \sqrt{\frac{\Sigma x^2 - ((\Sigma x)^2/n)}{n-1}}$$

where

$\sum x^2$ is the sum of the squares of individual measurements
$\sum x$ is the sum of individual measurements
is the number of individual measurements

$$= \frac{\text{Mass of solute (g)}}{100\,\text{g solution}} \times 100\%$$

Although precision or reproducibility of analysis can be expressed in terms of the standard deviation, the magnitude of the analyte in the sample may alter the standard deviation quite significantly. This is shown in Examples 2.1 and 2.2.

EXAMPLE 2.1

The total petroleum hydrocarbons (TPH) in an effluent sample in six replicate analyses were found to be as follows: 5.3, 4.9, 5.1, 5.5, 4.7, and 5.0 mg/L.

Determine the standard deviation.

$$\Sigma x = 30.5; \quad \Sigma x^2 = 155.45$$

x	x^2
5.3	28.09
4.9	24.01
5.1	26.01
5.5	30.25
4.7	22.09
5.0	25.00
30.5	155.45

$$(\Sigma x)^2 = (30.5)^2 = 930.25;\ n = 6$$

$$s = \sqrt{\frac{155.45 - (930.25/6)}{6-1}} = \sqrt{\frac{0.41}{5}} = 0.29\ \text{mg/L}$$

EXAMPLE 2.2

If the results of six replicate analyses for TPH in an influent sample were 10 times greater (i.e., 53, 49, 51, 55, 47, and 50 mg/L), the standard deviation would be as follows:

$$\Sigma x = 305; \quad \Sigma x^2 = 15,545$$

$$(\Sigma x)^2 = 93,025;\ n = 6$$

$$s = \sqrt{\frac{15,545 - (93,025/6)}{5}}\ \text{mg/L} = 2.86\ \text{mg/L}$$

A further increase in the magnitude of analyte concentrations as 530, 490, 510, 550, 470, and 500 mg/L on replicate analysis would give a standard deviation of 28.6 mg/L. Thus, standard deviation, which varies with the magnitude or size of the measurements, has no meaning unless the magnitude of the analyte concentrations is stated.

In other words, the precision of analysis will always be very low for any influent sample relative to the corresponding effluent sample. This may cause some confusion that would not arise if the precision were expressed in other scales for which the analyte size need not be stated. One such scale is the relative standard deviation (RSD) or the coefficient of variance (CV), which is a ratio of standard deviation to the arithmetic mean of the replicate analyses and expressed as a percentage

$$\text{RSD} = \left(\frac{s}{\bar{x}}\right)100\%$$

In Examples 2.1 and 2.2, the RSDs are as follows:

$$\frac{0.29\ \text{mg/L}}{5.3\ \text{mg/L}} \times 100\% = 5.4\%$$
$$\frac{2.86\ \text{mg/L}}{53\ \text{mg/L}} \times 100\% = 5.4\%$$

Thus, the RSDs in the replicate analyses of the influent and effluent samples with 10 times variation in magnitude remain the same at 5.4%, while their standard deviations are 0.29 and 2.8 mg/L, respectively.

Another scale of measurement of precision is the standard error of mean (M), which is the ratio of the standard deviation to the square root of the number of measurements (n)

$$M = \frac{s}{\sqrt{n}}$$

The standard error of mean, M, however, would also vary in the same proportion as the standard deviation relatively with the size of the analyte in the sample.

In routine tests of environmental samples, many repeat analyses of sample aliquots are not possible. The precision, therefore, is measured from duplicate and multiple analyses of the sample aliquots and expressed as the relative percent difference (RPD). The RPD is determined from the duplicate analysis performed under identical conditions on two aliquots of one of the samples in a batch and is calculated by dividing the difference of the test results with the average of the test results and expressed as a percentage. Thus,

$$\text{RPD} = \left[(a_1 - a_2) \text{ or } \frac{(a_2 - a_1)}{\{(a_1 + a_2)/2\}}\right] \times 100$$

where a_1 and a_2 are the results of the duplicate analysis of a sample.

EXAMPLE 2.3

Concentrations of chloride in two aliquots of a sample were found to be 9.7 and 11.1 mg/L. Determine the precision of analysis as RPD

$$\text{RPD} = \frac{(11.1\,\text{mg/L} - 9.7\,\text{mg/L})}{(11.1\,\text{mg/L} + 9.7\,\text{mg/L})/2} \times 100\%$$
$$= \frac{(1.4\,\text{mg/L})}{10.4\,\text{mg/L}} \times 100\% = 13.5$$

Accuracy determines the closeness of the analytical data to the true value. It is estimated from the recovery of a known standard spiked into the sample. Based on the percent spike recovery, a correction for the bias may be made. Routine environmental analyses generally do not require such corrections in the results. However, in specific types of analysis, correction for bias may be required when the percent spike recovery for a QC batch sample is greater than 0 and less than 100. In the wastewater analyses of certain organics, U.S. EPA has set forth the range for percent recovery. If the spike recovery for any analyte falls outside the range, the QC criteria for that analyte is not met and the problem needs to be identified and corrected before performing further analysis.

The matrix spike recovery may be defined in two different ways: (1) one method determines the percent recovery only for the standard added to the spiked sample, as followed by U.S. EPA and (2) the other method calculates the percent recovery for the combined unknown sample and the standard. Spike recovery calculated by both these methods would give different values.

Definition 2.3.1

U.S. EPA Percent Recovery Formula

$$\%\ \text{Recovery} = \frac{100(X_s - X_u)}{K}$$

where
X_s is the measured value for the spiked sample
X_u is the measured value for the unspiked sample adjusted for dilution of the spike
K is the known value of the spike in the sample

Definition 2.3.2

$$\%\ \text{Recovery} = \frac{\text{Measured concentration}}{\text{Theoretical concentration}} \times 100\%$$

Theoretical concentration can be calculated as

$$\frac{(C_u \times V_u)}{(V_u + V_s)} + \frac{(C_s \times V_s)}{(V_u + V_s)}$$

where
C_u is the measured concentration of the unknown sample
C_s is the concentration of the standard

while
V_u and V_s are the volumes of the unknown sample and standard, respectively

The percent spike recovery as per either definition may be calculated by taking either the concentration or the mass of the analyte into consideration. This is shown in Examples 2.4 through 2.6.

EXAMPLE 2.4

A wastewater sample was found to contain 3.8 mg/L cyanide. A 100 mL aliquot of this sample was spiked with 10 mL of 50 mg/L cyanide standard solution. The concentration of this spiked solution was measured to be 8.1 mg/L.

1. Calculate the percent spike recovery as per Definition 2.3.1.
   a. Calculation based on concentration:

$$X_s = 8.10\ \text{mg/L}$$
$$X_u = \frac{(3.8\ \text{mg/L})(100\ \text{mL})}{110\ \text{mL}} = 3.454\ \text{mg/L}$$
$$K = \frac{(50\ \text{mg/L})(10\ \text{mL})}{110\ \text{mL}} = 4.545\ \text{mg/L}$$
$$\%\ \text{Recovery} = \frac{8.10\ \text{mg/L} - 3.454\ \text{mg/L}}{4.545\ \text{mg/L}} \times 100\%$$
$$= 102.2\%$$

   b. Calculation based on mass (alternative method): The total mass of CN^- ions in 110 mL of sample and spike solution

$$= \frac{8.1\,\text{mg}}{L} \times 0.110\,\text{L} = 0.891\,\text{mg}.$$

The mass of CN^- ions present in 100 mL of sample aliquot before spiking

$$= \frac{3.8\text{ mg}}{L} \times 0.100\text{ L} = 0.380\text{ mg}.$$

The mass of CN^- ions in 10 mL standard solution spiked

$$= \frac{50\text{ mg}}{L} \times 0.01\text{L} = 0.500\text{ mg}$$

$$\%\text{ Recovery} = \frac{(0.891\text{mg} - 0.380\text{ mg})}{0.500\text{ mg}} \times 100$$
$$= 102.2\%.$$

2. Calculate the percent spike recovery as per Definition 2.3.2.
   a. Calculation based on concentration. Measured concentration of CN^- after spiking = 8.1 mg/L. Actual concentration of CN^- expected after the sample aliquot was spiked

$$= \text{Initial concentration of } CN^- \text{ in the aliquot}$$
$$+ \text{ Concentration of } CN^- \text{ in the spike standard}$$
$$= \frac{(3.8\text{ mg/L})(100\text{ mL})}{(110\text{ mL})} + \frac{(50\text{ mg/L})(10\text{ mL})}{(110\text{ mL})}$$
$$= 8.00\text{ mg/L}$$
$$\%\text{ Recovery} = \frac{8.10\text{ mg/L}}{8.00\text{ mg/L}} \times 100$$
$$= 101.2$$

   b. Calculation based on mass (alternative method).
   Measured amount of cyanide in a total volume of 110 mL (sample + spike)

$$8.1\text{mg/L} \times 0.110\text{ L} = 0.891\text{mg}$$

The actual amount of cyanide that is expected in 110 mL of the sample and spike solution

$$(3.8\text{ mg/L} \times 0.100\text{ L}) + (50\text{ mg/L} \times 0.01\text{L}) = 0.880\text{ mg}$$

$$\%\text{ Recovery} = \left(\frac{0.891\text{mg}}{0.880\text{ mg}}\right) \times 100\% = 101.2\%$$

EXAMPLE 2.5

A sample measured 11.7 mg/L. A 50 mL portion of the sample was spiked with 5 mL of 100 mg/L standard. The result was 18.8 mg/L. Calculate the spike recovery as per Definitions 2.5.1 and 2.5.2. (Calculations are based on concentrations.)

Definition 2.5.1

$$X_s = 18.8 \text{ mg/L}$$

$$X_u = \frac{(11.7 \text{ mg/L})(50 \text{ mL})}{55 \text{ mL}} = 10.64 \text{ mg/L}$$

$$K = \frac{(100 \text{ mg/L})(5 \text{ mL})}{55 \text{ mL}} = 9.09 \text{ mg/L}$$

$$\% \text{ Recovery} = \frac{18.80 \text{ mg/L} - 10.64 \text{ mg/L}}{9.09 \text{ mg/L}} \times 100 = 89.8\%$$

Definition 2.5.2

$$\text{Measured concentration} = 18.8 \text{ mg/L}$$

$$\text{Actual concentration} = \frac{(11.7 \text{ mg/L})(50 \text{ mL})}{55 \text{ mL}} + \frac{(100 \text{ mg/L})(5 \text{ mL})}{55 \text{ mL}} = 19.7 \text{ mg/L}$$

$$\% \text{ Recovery} = \frac{18.8 \text{ mg/L}}{19.7 \text{ mg/L}} \times 100 = 95.3\%$$

When the spike recovery is less than 100%, U.S. EPA formula (Definition 2.5.1) gives a *lower* value than that calculated as per Definition 2.5.2, as we see in Example 2.5. However, if the recovery is above 100%, Definition 2.5.1 formula gives a *higher* value (Example 2.4).

Unlike aqueous samples, spike recovery for soil and solid wastes often does not require any correction to be made in the volume of the spike solution. Because the analysis of all soil and solid matrices requires that the analyte in the solid sample be extracted into a definite volume of solvent, there is no need to make any volume or mass correction for the spike in the added solution. This is shown in Example 2.6.

EXAMPLE 2.6

A soil sample was Soxhlet extracted with Freon and the extract was analyzed for petroleum hydrocarbons (PHC) by IR spectrometry. The concentration of PHC in the sample was found to be 285 mg/kg. A 40 g portion of this sample was spiked with 2 mL of 1000 mg/L PHC standard. The concentration of the spiked sample was measured as 326 mg/kg. Determine the accuracy of the analysis as the percent recovery of the amount spiked.

The mass of PHC in the spiked sample

$$= 40 \text{ g} \times \frac{326 \text{ mg}}{1000 \text{ g}} = 13.04 \text{ mg}.$$

The mass of PHC in the sample before spiking

$$= 40 \text{ g} \times \frac{285 \text{ mg}}{1000 \text{ g}} = 11.40 \text{ mg}.$$

$$\text{Amount Spiked} = 2 \text{ mL} \times \frac{1000 \text{ mg}}{1000 \text{ mL}} = 2.00 \text{ mg}$$

$$\% \text{ Recovery} = \frac{13.04 \text{ mg} - 2.00 \text{ mg}}{11.40 \text{ mg}} = 96.8\%$$

The mass of the spiked sample is considered as 40 g and not 43 g (to include the mass of 2 mL of the spiking solution with an approximate density 1.5 g/mL) in the above calculation. This is true because this 2 mL of solvent that is added onto the soil as a spike standard readily mixes into the Soxhlet extract. Therefore, the mass of the sample after extraction (i.e., the mass of the solid residue) almost remains the same as it was before its extraction.

The percent spike recovery in the above example may alternatively be determined by the U.S. EPA formula as shown below:

$$X_s = 326 \text{ mg/kg}; X_u = 285 \text{ mg/kg}$$

$$K = \left[\frac{(2 \text{ mL} \times 1000 \text{ mg}/1000 \text{ mL})}{40 \text{ g}}\right] \times \frac{1000 \text{ g}}{1 \text{kg}} = 50 \text{ mg/kg}$$

$$\% \text{ Recovery} = \frac{(326 \text{ mg/kg} - 285 \text{ mg/kg})\,100}{50 \text{ mg/kg}} = 82.0\%$$

No mass or volume correction is made in the above calculation involving solid samples. Thus, X_u was considered as 285 mg/kg.

The percent spike recovery in the above example employing Definition 2.5.2 would then be

$$\frac{(326 \text{ mg/kg})}{(285 \text{ mg/kg}) + (50 \text{ mg/kg})} \times 100 = 97.3\%$$

In the organic analysis, in addition to the matrix spike (which means adding a measured amount of one or more of the same substances that are analyzed for), a few surrogate substances are also spiked onto the sample. Surrogates are compounds that have chemical properties that are similar to those of analytes but are not found in the environmental matrices. Deuterated or fluoro-substituted analogs of the analytes, such as phenol-d_6, nitrobenzene-d_5, or pentafluorobenzene, etc. are examples of surrogates. Surrogate spike recovery indicates extraction efficiency and measures the accuracy of the method as a whole. Surrogates for specific classes of analytes are listed in Section II under their respective group headings.

CONTROL CHARTS

There are two types of control charts: accuracy charts and precision control charts. Accuracy control charts are prepared from the percent spike recoveries data obtained from multiple routine analyses. Precision control charts may be prepared from the RPD of analyte concentrations in the samples and their duplicate analytical data. Alternatively, RPDs are calculated for percent recoveries of the analytes in the matrix spike and matrix spike duplicate in each batch and 20 (or any reasonable number of data points) are plotted against the frequency or number of analysis. If the samples are clean and the analytes are not found, the aliquots of samples must be spiked with the standard solutions of the analytes and the RPD should be determined for the matrix spike recoveries. Ongoing data quality thus can be checked against the background information of the control chart. Sudden onset of any major problem in the analysis can readily be determined from the substantial deviation of the data from the average.

Thus, control charts measure both the precision and accuracy of the test method. A control chart is prepared by spiking a known amount of the analyte of interest into four to six portions of reagent grade water. The recoveries are measured and the average recovery and standard deviation are calculated. In routine analysis, one sample in a batch is spiked with a known concentration of a standard and the percent spike recovery is measured. An average of 10–20 such recoveries is calculated and the standard deviation about this mean value is determined. The spike recoveries are

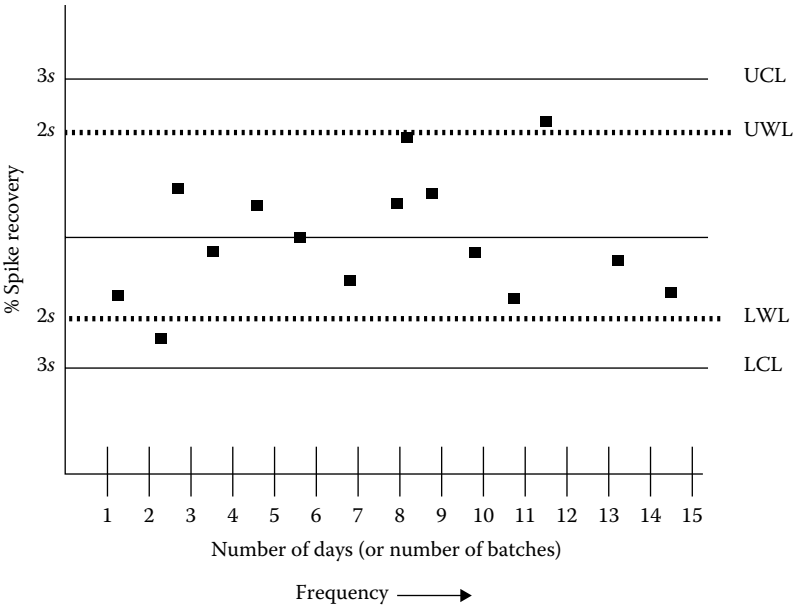

FIGURE 2.2 Accuracy control chart.

plotted against the frequency of analysis or the number of days. A typical control chart is shown in Figure 2.2.

The upper and lower warning limits (UWL and LWL) are drawn at 2*s* above and below, respectively, of the mean recovery. The UCL and LCL are defined at the 3*s* value about the mean. If any data point falls outside the UCL or LCL, an error in analysis is inferred that must be determined and corrected. The recoveries should fall between both the warning limits (UWL and LWL). Similarly, seven data points falling consecutively above or below the mean should indicate an analytical error. In addition, two-thirds of the number of points should fall within one standard deviation of the mean.

The control charts of the type discussed above measure both the accuracy and the precision of the analysis. The accuracy, however, is not well defined. For example, if the calibration standards were mistakenly prepared from a wrong stock solution (of wrongly labeled concentration), the true value of spike recoveries for the whole set of data would be different. Theoretically, another drawback of this concept is that the standard deviation windows (i.e., 2*s* and 3*s* about the mean) cannot be fixed and would continuously change as the mean would change with the addition of each data point. In addition, there is an element of bias in our interpretation favoring the initial results over the latter results, that is, the quality of data rests on assuming a high accuracy of initial data in the control chart. Despite these minor drawbacks, control charts are very useful in assessing data quality in environmental analysis.

Alternatively, precision control charts may be constructed by plotting the RPDs of duplicate analyses measured in each analytical batch against the frequency of analysis (or number of days). The mean and the standard deviation of an appropriate number (e.g., 20) of RPDs are determined. The UWL and LWL and the UCL and LCL are defined at 2*s* and 3*s*, respectively. Such a control chart, however, would measure only the quality of precision in the analysis. This may be done as an additional precision check in conjunction with the spike recovery control chart.

Thus, control charts are key ingredients of QC programs in environmental analysis.

3 Analysis of Organic Pollutants by Gas Chromatography

GC is the most common analytical technique for the quantitative determination of organic pollutants in aqueous and nonaqueous samples. In environmental analysis, a very low detection limit is required to determine the pollutants at trace levels. Such low detection can be achieved by sample concentration followed by cleanup of the extract to remove interfering substances. Sample extractions and cleanup procedures are described in detail in Chapter 5.

The GC methods, however, can be applied only to determine the presence and quantifications of any specific substance of interest. On the other hand, it cannot be used to identify an absolutely unknown substance which is a limitation of the GC technique. Despite such limitations, GC is an excellent tool for environmental analysis because the list of pollutants to be measured is confined to small numbers for which the compounds in their neat form or certified analytical standard solutions are commercially available. The presence of any substance of interest eluted as a peak in the chromatogram can be confirmed from its retention time matching with that of the same substance in its known standard solution. Furthermore, the retention times of the peaks also have to match identically as well on an alternate GC column to prevent any false identification. Also, there are additional techniques to confirm the presence of a substance if doubt arises on its presence. Some of these techniques are discussed below. There are two other limitations of GC methods that may be cited here. One is the difficulty in separating isomers in many cases, for example, *ortho*- and *para*-xylenes or anthracene and phenanthrene. Also, the substances that have high molecular weights, such as chlorophyll, cannot be determined by GC methods. However, as mentioned earlier, by using appropriate columns, detectors, and chromatographic conditions, a vast number of organic substances, including most environmental organic pollutants, can be conveniently screened and quantified by GC methods.

Aqueous samples containing volatile organics can be directly analyzed by GC (without any separate sample extraction steps) interfaced with a purge and trap setup. The analytes in the sample are concentrated by the purge and trap technique, as discussed in the following section, prior to their analysis by GC or GC/MS. The volatile organics in soils, sediments, and solid wastes may be analyzed in a similar way by subjecting an aqueous extract of the sample to purge and trap concentration. Alternatively, the analytes may be thermally desorbed from the solid matrices and transported onto the GC column by a carrier gas.

At the outset, one must understand certain principles of GC to assess if it is a proper analytical tool for the purpose. If it is so, how do we achieve the best separation and identification of component mixtures in the sample with reasonable precision, accuracy, and speed? In addition, what kind of detector and column should be selected for the purpose? It is, therefore, important to examine the type of compounds that are to be analyzed and certain physical and chemical properties of these compounds. Information regarding the structure and the functional groups, elemental composition, the polarity in the molecule, its molecular weight, boiling point, and thermal stability are very helpful for achieving the best analysis. After we know these properties, it is very simple to perform the GC analysis of component mixtures. To achieve this, just use an appropriate column and a proper detector. Properties of columns and detectors are highlighted in the following sections.

The efficiency of the chromatographic system can be determined from the number of theoretical plates per meter. Although this term primarily describes the property and resolution efficiency of a

column, other extra column variables, such as the detector, inlet, injection technique, and the carrier gas velocity can also affect the theoretical plates. This is calculated from the following equation:

$$\text{Theoretical plates/m} = \frac{5.54\left(\frac{t}{w}\right)^2}{L}$$

where

t is the retention time of the test compound
w is the width of the peak at half height
L is the length of the column (m)

The number of theoretical plates also depends on the partition ratio k of the test compound and its solubility in the liquid phase. Substances that have higher k values have lower plate numbers. Greater plate numbers indicate greater resolution or better separation of the component mixture.

SELECTION OF COLUMN

A variety of GC columns are commercially available to meet the specific purpose. The selection of columns, their stationary phases, inside diameters, lengths, and the film thickness are briefly discussed below.

A capillary column is usually preferred over a packed column for better resolution and lower detection limit. The efficiency of a column to separate organic compounds depends on the stationary phase and the polarity of the analyte molecules. The polarity of the phase, therefore, is the most important characteristic in selecting a column. While a nonpolar phase most effectively separates nonpolar molecules, a polar phase is required to achieve the separation of polar compounds. Aliphatic hydrocarbons containing C−H single bonds are all nonpolar compounds while those containing carbon–carbon double bonds, such as olefins and aromatics, are polarizable compounds. On the other hand, organic compounds containing oxygen, nitrogen, sulfur, phosphorus, or halogen atoms should exhibit greater polarity. Examples of such polar compounds include carboxylic acids, ketones, aldehydes, esters, alcohols, thiols, ethers, amines, nitroaromatics, nitrosamines, nitriles, halocarbons, PCBs, and organic phosphates. An increase in polarity reduces the thermal stability of the stationary phase. Therefore, a phase of least polarity should be selected, whenever possible, to enhance the life of the column. Table 3.1 lists the polarity of various stationary phases of common capillary GC columns.

Capillary columns are composed of fused silica that has shown remarkable properties of inertness and efficiency in chromatographic analysis. Glass capillaries and stainless steel are sometimes used too; but their applications are nowadays limited.

The inside diameter of the capillary column is another major factor that often dictates the separation of components. The narrowbore columns with internal diameter (ID) 0.20, 0.25, and 0.32 mm provide the best separation for closely eluting components and isomers. The smaller the ID, the greater is the resolution. On the other hand, a major disadvantage of such a narrowbore column, however, is its low sample capacity (i.e., the quantity of sample that can be applied without causing the peak(s) to overload). Wider bore columns of 0.53 and 0.75 mm ID do not have this problem. These wider columns have greater sample capacity than narrowbore columns but relatively lower resolution capacity. Such widebore columns, however, are better suited for environmental samples that often contain pollutants at high concentrations. In addition, widebore columns of 0.53 and 0.75 mm ID provide sufficient sensitivity for minor components' peaks without being overloaded with the major components. The sample capacity of a column may further be increased by temperature programming. It also depends on the polarity of the components and the phase—the polar

phase has a high capacity for polar components, while the nonpolar phase has a high capacity for nonpolar components (Table 3.1).

The stationary phase can be bound to the tubing either as a physical coating on the wall, or can be chemically immobilized. The former type phases are called nonbonded phases, while the chemically bound phases, cross-linked within the tubing, are known as bonded phases. The latter is preferred because it can be used at high temperatures with less bleeding and can be rinsed with solvents to remove nonvolatile substances that accumulate on the column.

The film thickness of the stationary phase is another major factor that should be taken into account for column selection. A thicker film increases the resolution on a nonpolar column, but decreases the same on a polar column. It also increases the sample capacity, retention of sample components, and, therefore, the retention time and the temperature at which the components would elute from the column and the column bleed. Thus, it has both advantages and disadvantages. A thicker film (>1 μm) should be used to analyze gases or substances with low boiling points or to analyze highly concentrated samples. On the other hand, a thin film (<0.25 μm) should be used to analyze compounds with high boiling points (>300°C) and should be employed with a shorter column (10–15 m length). Film thickness of the stationary phase and the column ID are interrelated, as follows:

$$\text{Phase ratio}, \beta = \text{column radius}, \mu\text{m}/\text{phase thickness}$$

Columns with equal beta value (β) will provide similar separations under the same analytical conditions. For example, a capillary column with 0.32 μm ID and 0.8 μm phase film thickness could be substituted with a column of the same phase with 0.53 μm ID and 1.3 μm film thickness to produce very similar separation. However, standard film thickness (0.25–0.8 μm) should work for most chemical analyses.

Separation of closely eluting components can be efficiently achieved on a longer column. The greater the length of the capillary column, the higher is its resolution efficiency. On the other hand, the long column enhances the time of analysis, increasing the retention times of the components. As mentioned earlier, high resolution can also be attained with narrowbore columns. Therefore, optimizing the column length and ID can provide good separation in the desired analysis time.

TABLE 3.1
Polarity of Stationary Phases

Polarity	Stationary Phase	Examples
Nonpolar	Polydimethylsiloxane	AT-1, BP-1, DB-1, DC-200, HP-1, OV-1, OV-101, RSL-160, Rtx-1, SF-96, SP-2100, SPB-1, ULTRA-1
	Polyphenylmethylsiloxane	AT-5, BP-5, DB-5, HP-5, MPS-5, OV-73, RSL-200, Rtx-5, SE-52, SPB-5, ULTRA-2
Intermediate	Polyphenylmethylsiloxane	AT-20, BP-10, DB-17, HP-17, MPS-50, OV-17, RSL-300, Rtx-20, SP-2250, SPB-20
	Polycyanopropylphenyldimethylpolysiloxane	AT-1301, DB-1301, Rtx-1301
	Polycyanopropylphenylmethylsiloxane	AT-1701, DB-1701, GB-1701, OV-1701, Rtx-1701, SPB-1701
Polar	Polytrifluoropropylsiloxane	AT-210, DB-210, OV-210, QF-1, RSL-400, SP-2401
	Polyphenylcyanopropylmethylsiloxane	AT-225, DB-225, HP-225, OV-225, RSL-500, Rtx-225
	Polyethyleneglycol	AT-WAX, BP-20, Carbowax 20M, CP/WAX 51, DB-WAX, HP-20M, Stabilwax, Supelcowax 10, Superox II
Very polar (acidic)	Polyethyleneglycol ester	AT-1000, FFAP, Nukol, OV-351, SP-1000, Superox-FA

TABLE 3.2
Separation Efficiency and Sample Capacity of GC Columns of Varying IDs

Column ID (mm)	Sample Capacity (ng)	Separation Efficiency (Theoretical Plates/m)[a]	Carrier Gas Flow Rate, Optimum (cc/min)
		Capillary	
0.20	10–30	5000	0.4
0.25	50–100	4200	0.7
0.32	400–500	3300	1.4
0.53	1000–2000	1700	2.5
0.75	10,000–15,000	1200	5
		Packed	
2.0	20,000	2000	20

Note: The data presented are for a 60 m capillary column and a 2 m packed column.
[a] Numbers are rounded off. The higher this number, the greater is the resolution efficiency.

The separation efficiency of a column can be alternatively determined from the number of theoretical plates per meter. The greater the number, the greater is the resolution efficiency of the column. Table 3.2 presents the separation efficiency and the sample capacity of GC columns of varying IDs.

DETECTORS

Selection of GC detectors is very crucial in chemical analysis. Flame ionization detector (FID) and thermal conductivity detector (TCD) can be used for all general purposes. However, the detection limits for analytes are high, especially for the TCD. The latter is commonly used for gas analysis.

When using FID, aqueous samples can be directly injected onto the GC without any sample extraction. The detection limit of an analyte, however, in such a case would be much higher (low ppm level) than what is desired in environmental analysis. When appropriate sample concentration steps are adopted, organic compounds in aqueous and solid matrices and air can be effectively determined at a much lower detection level. Carbon disulfide is commonly used in the air analysis of many organics by GC-FID.

Halogen-specific detectors, such as the electron capture detector (ECD) and Hall electrolytic conductivity detector (HECD) show the best response to compounds that contain halogen atoms. The nitrogen–phosphorus detector (NPD) in the nitrogen mode can determine most nitrogen-containing organics while the same detector in the phosphorus-specific mode can analyze organophosphorus compounds. The flame photometric detector (FPD) is also equally efficient for determining phosphorus compounds. The FPD, however, is primarily used to analyze sulfur-containing organics. The photoionization detector (PID) is sensitive to substances that contain the carbon–carbon double bond such as aromatics and olefins, as well as their substitution products.

CALIBRATION

Prior to the analysis of the unknown, a calibration standard curve is prepared by running at least four standards. Calibration is performed in two ways: the external standard method and internal standard method. The external standard method involves preparation of a calibration curve by plotting the area or height response against concentrations of the analyte(s) in the standards. The calibration factor is then calculated as the ratio of concentrations to area/height response and should be constant over a wide range of concentrations. To determine the concentration of the analyte in

the unknown sample (extract), the response for the unknown should be compared with that of the standards within the linear range of the curve. Alternatively, an average of response ratios may be calculated which is compared with the response of the analyte. A single point calibration may be used if the area/height response of the analyte is within ±20% of the response of the standard.

The internal standard method is more reliable than the external standard method. Equal amounts of one or more internal standards are added onto equal volumes of sample extracts and the calibration standards. The response factor (RF) is then calculated as follows:

$$\mathrm{RF} = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where A_s and A_{is} are the area (or height) response for the analyte and the internal standard, respectively; while C_s and C_{is} are their concentrations. Thus, the RF for analytes may be determined by running standard solutions of the analytes containing internal standards. If the RF values over the working range of concentrations fall within ±20% of relative standard deviation, an average RF value should be used in the above equation to determine the concentration of the analytes in the sample. Alternatively, a calibration curve may be plotted between response ratio (A_s/A_{is}) versus RF.

The concentration of the analyte in the sample $= A_s \times C_{is} \times D/A_{is} \times \mathrm{RF}$ where D is the dilution factor. For aqueous samples, the concentration of the analyte is usually expressed in μg/L. All concentration terms including those of the calibration standards and internal standards must be in the same unit.

Calculations

The concentration of an analyte in an aqueous or nonaqueous sample may be calculated by one of the following methods.

External Standard Calibration

The area/height response for the analyte peak is compared with that of the standards from the calibration curve or from the calibration factor.

$$\text{Concentration, } \mu\text{g/L} = \frac{A_{unk} \times Q_{std} \times V_{tot} \times D}{A_{std} \times V_{inj} \times V_{sample}}$$

where

A_{unk} is the area count or peak height of the analyte
Q_{std} is the amount of standard injected or purged in ng
V_{tot} is the volume of total extract in μL
D is the dilution factor, dimensionless
A_{std} is the area or peak response for the standard
V_{inj} is the volume of extract injected in μL
V_{sample} is the volume of sample extracted or purged in mL

For nonaqueous samples, the concentration of the analyte is calculated in the same way except that the weight of the sample W is substituted for the volume of the sample, V_{sample}. Thus,

$$\text{Concentration, } \mu\text{g/kg} = \frac{A_{unk} \times Q_{std} \times V_{tot} \times D}{A_{std} \times V_{inj} \times W}$$

The concentration calculated above is on the sample "as is" and not as dry weight corrected. Concentration on a dry weight basis may be calculated by dividing the above result with the percent total solid expressed as a decimal.

EXAMPLE 3.1

A 500-mL sample aliquot was extracted with hexane to a final volume of 2 mL. The volume of sample extract and the standard injected were 4 μL. The concentration of the analyte in the standard was 50 μg/L. The area response of the analyte in the sample extract and the standard solutions were 28,500 and 24,800, respectively. Determine the concentration of the analyte in the sample.

$$A_{unk} = 28{,}500$$
$$A_{std} = 24{,}800$$
$$Q_{std} = 4\,\mu L \times \frac{50\,\mu g}{1L} \times \frac{1L}{1{,}000{,}000\,\mu L} \times \frac{1000\,ng}{1\mu g} = 0.2\,ng$$
$$V_{tot} = 2\,mL \times \frac{1000\,\mu L}{1mL} = 2000\,\mu L$$
$$V_{inj} = 4\,\mu L$$
$$V_{sample} = 500\,mL$$
$$D = 1, \text{ the extract was not diluted}$$

Concentration of the analyte in the sample, μg/L

$$= \frac{28{,}500 \times 0.2\,ng \times 2000\,\mu L \times 1}{24{,}800 \times 4\,\mu L \times 500\,mL}$$
$$= 0.23\,ng/mL$$
$$= 0.23\,\mu g/L$$

Alternative Calculation

When the aliquots of the sample extract and the standard injected into the column are the same (i.e., 4 μL), the concentration of the analyte in the sample may be calculated in a simpler way as shown below:

$$\text{Concentration of analyte, } \mu g/L = \frac{(C_{extract} \times V_{extract} \times D)}{V_{sample}}$$

where

$C_{extract}$ is the concentration of the analyte, μg/L in the extract determined from the calibration standard curve
$V_{extract}$ is the volume of extract, mL
V_{sample} is the volume of sample, mL
D is the dilution factor

In the above problem the concentration of the analyte in the *extract* is

$$\frac{28{,}500}{24{,}800} \times 50\,\mu g/L = 57.5\,\mu g/L$$

(taking single point calibration) which can also be determined from the external standard calibration curve. Therefore, the concentration of the analyte in the *sample*

$$= 57.5\,\mu g/L \times \frac{2\,mL}{500\,mL} \times 1$$
$$= 0.23\,\mu g/L.$$

Internal Standard Method

The concentration of the analyte can be determined from the RF using the equation

$$C_s = \frac{A_s \times C_{is}}{A_{is} \times RF}$$

For this, the internal standard eluting nearest to the analyte should be considered.

ROUTINE ANALYSIS

Routine GC analysis for environmental samples involve running one of the calibration check standards before sample analysis to determine if the area or height response is constant (i.e., within 15% of standard deviation of the RF or calibration factor, and to check if there is a shift in the retention times of the analytes' peaks). The latter can occur to a significant degree due to any variation in conditions, such as temperature or the flow rate of the carrier gas. Therefore, an internal standard should be used, if possible, in order to determine the retention time shift or to compensate for any change in the peak response. If an analyte is detected in the sample, its presence must be ascertained and then confirmed as follows:

1. Peak matching of the unknown with the known should be done, additionally, at a different temperature and/or flow rate conditions.
2. The sample extract should be spiked with the standard analyte solution at a concentration to produce a response that is two to three times the response of the unknown peak.
3. The identification of the peak must be finally confirmed on a second GC column. This may be done either after performing Steps 1 and 2 or by injecting the extract straight onto the second column (confirmatory GC column) without going through Steps 1 and 2.

In addition to determining the presence or absence of pollutants of interest in the sample, the routine analysis must include QC/quality assurance tests to determine the precision and accuracy of the test results and any possible source of errors such as sample contamination, absence of preservative, or exceeding of sample holding time. The QA/QC is discussed at length in Chapter 2.

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4 Analysis of Organic Pollutants by Gas Chromatography/ Mass Spectrometry

GC/mass spectroscopy (GC/MS) is probably the best technique to identify a wide array of unknown organic substances in sample matrices. It is also the most positive confirmatory test to determine the presence of pollutants in the sample. Its application in environmental analysis has grown enormously in the last decade.

The method is based on the principle of chromatographic separation of components of a mixture on a GC column, followed by their identification from their mass spectra. The compounds are separated on a suitable GC column, following which the components eluted from the column are subjected to electron-impact or chemical ionization (CI). The fragmented and molecular ions are identified from their characteristic mass spectra. Thus, the substances present in the sample are determined from their characteristic primary and secondary ions and from their retention times. Some common mass spectral terms are briefly explained below along with their definitions. Readers further interested in the subject may refer to the bibliographic citations at the end of this chapter (APHA, AWWA, and WEF, 2005; Field et al., 2002; Kebbekus and Mitra, 1998; Patnaik, 2004; U.S. EPA, 1992).

TERMS AND DEFINITIONS

The ***m/z*** or the mass-to-charge ratio is the ratio of the mass number of a particle to the number of electrostatic charge unit(s) on it; such a charge unit is usually one. For example, if the *m/z* is 76, the mass of the particle or the fragmented ion is 76.

The **mass spectra** are a plot of such *m/z* in *x*-axis versus their abundance or relative intensity. Every compound has its characteristic mass spectra indicating the masses of the fragments of the molecule and/or the intact molecule itself and their abundances or the relative amounts.

The term **primary characteristic mass ion** refers to the peak that has the most abundant mass in the mass spectra of a compound. A compound may often be identified and quantified from its primary mass ion.

The **secondary mass ions** are the other major peaks in the mass spectra of a compound. The *m/z* abundances of such secondary ions resulting from miscellaneous fragmented moieties of a compound must always be lower than that of its primary mass ion.

The term **amu** is the abbreviation of atomic mass unit. It is based on a relative scale in which the carbon-12 isotope (^{12}C) is assigned exactly a value of 12 amu. (1 amu = 1 dalton [Da].)

The **molecular ion**, M^+, results from the ionization of the intact molecule. The *m/z* of the molecular ion should be equal to the molecular mass of the compound.

The **base peak** refers to the most intense peak in the mass spectra with *m/z* of highest abundance. It is arbitrarily assigned a value of 100% intensity in the mass spectra (in the plot showing *m/z* against their % relative intensity).

APPLICATION OF MASS SPECTROMETRY

The single-most important application of mass spectrometry (MS) is of course to identify an unknown compound from its characteristic mass spectra. The compounds are identified from their

molecular mass ions wherever possible, and from their primary and secondary mass ions as well along with the retention times of the compound peaks. It is therefore not required to run the same sample or the sample extract on an alternate column as is done with the GC analysis to confirm the presence of a compound. The MS may also be applied to quantify compounds at trace concentrations. Although a mass selective detector is much less sensitive to most GC or LC detectors, various techniques, however, may be applied to improve the detection limits. The instrument detection limits for many compounds usually fall in the range of lower parts per million, but that, however, may depend on the nature of the compound. A compound may be identified and measured under the selective ion monitoring (SIM) mode where the primary and secondary characteristic mass ions are looked for and their *m/z* abundances are used for quantification. This can lower the detection levels for the compounds. Among the other applications of MS are determining the molecular weights of compounds (from their molecular mass ions), and their molecular formulas, determining isotopes of elements, and carrying out kinetic studies to elucidate pathways of reactions. To derive the molecular formula of an unknown compound, the total number of C, H, O, and N atoms in the compound and the number of single, double, and triple bonds present in the molecule need to be calculated. This can be done using some established rules, some of which are briefly highlighted below. From the natural abundances of most common isotopes and often from the fragmentation patterns of various classes of compounds that are well established, the tasks of identifying an unknown substance from its mass spectra becomes relatively simple. It may be noted here that the mass spectral library search can often be misleading by inferring erroneous results or being inconclusive.

Interpretation of Mass Spectra

The interpretation of mass spectra requires some basic skill and knowledge of fragmentation of molecules. Some basic steps are discussed below. First, look for the molecular ion, M^+. If it appears it will be the highest *m/z* in the mass spectrum, except for the isotope peaks, such as $[M + 1]^+$, $[M + 2]^+$, etc. Also, other than the molecular ion M^+ look for the presence of the ions $[M + 1]^+$ for the ^{13}C and ^{15}N isotopes and similarly $[M + 2]^+$ for ^{18}O, ^{34}S, ^{37}Cl, and ^{81}Br ions. Note if the nominal mass is even or odd and apply the "nitrogen rule" discussed briefly below to determine if the molecule has an even mass and does contain 0 or an even number of N atom(s) or it has an odd mass and has an odd number of N atom(s). Try to calculate the molecular formula $C_xH_yN_zO_n$ where *x*, *y*, *z*, and *n* are the number of C, H, N, and O atom(s) in the formula, respectively. Then, determine the number of double bonds and rings in the molecule using the "index of hydrogen deficiency (IHD)" rule discussed very briefly below. With all such information, the structure of the compound can still be inconclusive. The most important step to interpret the structure, however, involves looking into the fragmentation of the molecule under electron impact ionization to account for the primary and secondary mass ions in the mass spectrum. When a molecule has a weak bond, it cleaves most easily. In addition, the stable fragments that may be ions, radicals, or neutral molecules tend to be formed most readily. Thus, the strong peaks in the mass spectrum may be attributed to fragmentation processes. Such fragmentation reactions may therefore provide useful information on the nature of the compounds, especially on their structural features and classes. Therefore, the fragmentation pattern reflected in the mass spectrum can indicate the fingerprint of the molecule. Some general fragmentation patterns are highlighted below.

Alkanes and alkyl side chains: cleavage of aliphatic carbon skeleton occurs at branch points because of the formation of more stable substituted carbocations, such as a tertiary carbocation and a neutral fragment.

Alkenes: $[R_1–CH=CH–CH_2–R_2]^+ \rightarrow R_1–CH=CH–CH_2^+$
(alkene loses—R_2 to give the allyl cation, $R_1–CH=CH–CH_2^+$)
Aromatics: $[C_6H_5–CH_2–R]^+ \rightarrow C_6H_5–CH_2^+ \rightarrow [C_7H_7]^+$

(alkyl benzenes give benzyl cation, $C_6H_5–CH_2$ that may rearrange to a seven-carbon ring, tropylium ion $[C_7H_7]^+$, the *m/z* for both is 91)
Amines: $[(R_1)(R_2)N–CH_2–R_3]^+ \rightarrow (R_1)(R_2)N^+=CH_2$
(amines lose the—R_3 free radical to give a quaternary N^+ ion)
Ketones and aldehydes: $[(R_1R_2)C=O]^+ \rightarrow R_1–C\equiv O^+$
(ketones and aldehydes tend to lose one of the alkyl groups to produce a stable acylium ion, $R_1–C\equiv O^+$ or $R_1–C^+=O$, cleavage occurs on the bond on the alpha C atom to the carbonyl group)
Ethers: $[R_1–CH_2–O–R_2]^+ \rightarrow R_1–CH=OH^+$
$[R_1–CH_2–O–R_2]^+ \rightarrow R_1–CH_2–O^{\bullet}$
$[R_1–CH_2–O–R_2]^+ \rightarrow CH_2=O^+–R_2$
(ethers are susceptible to cleave in three different ways as shown above, producing different types of primary ions)

Given below are some common fragments produced under the electron impact ionization resulting from the loss of neutral fragments. For example, ethoxybenzene, $C_6H_5OCH_2CH_3$ (mass 122) would lose an ethoxy group, $CH_3CH_2O–$ (mass 45) and therefore the mass spectrum should show two major peaks, one at *m/z* 77 (M−45) due to $C_6H_5–$ and the other at *m/z* 45 due to $CH_3CH_2O–$ fragments. In addition, there should be minor peaks at the *m/z* 29 and 93 corresponding to ethyl and phenoxy fragments, $CH_3CH_2–$ and $C_6H_5O–$, respectively. Similarly, propenyl bromide (bromopropene) should lose a bromine atom, *m/z* 79 and 81 (corresponding to isotopes ^{79}Br and ^{81}Br) showing mass peaks at 79, 81 for bromine and at 41 for M−Br, or the propenyl group ($C_3H_5–$).

M−1 (loss of a H atom)
M−15 (loss of a $–CH_3$ group)
M−16 (loss of an amino group, $–NH_2$, or an O atom (rare))
M−17 (loss of a H_2O molecule)
M−19 (loss of a F atom)
M−26 (loss of CH≡CH, or a cyanide group, –CN)
M−27 (loss of HCN)
M−28 (loss of $CH_2=CH_2$, CO)
M−29 (loss of an ethyl group, $–CH_2CH_3$, or HC(=O)–)
M−31 (loss of methoxy group, $CH_3O–$, or methanolic fragment $–CH_2OH$)
M−35 (loss of a chlorine atom, ^{35}Cl)
M−37 (loss of a chlorine atom, ^{37}Cl isotope)
M−42 (loss of $CH_2=CH–CH_3$, or $CH_2=C=O$)
M−43 (loss of a propyl group, $–C_3H_7$, or an acetyl group,$CH_3C(=O)–$)
M−45 (loss of an ethoxy group, $CH_3CH_2O–$)
M−46 (loss of a nitro group, $–NO_2$)
M−55 (loss of a butenyl group, $C_4H_7–$)
M−57 (loss of a propanoyl group, $CH_3CH_2C(=O)–$)
M−77 (loss of a phenyl group, $–C_6H_5$)
M−79 (loss of a bromine atom, ^{79}Br isotope)
M−81 (loss of a bromine atom, ^{81}Br isotope)
M−91 (loss of a benzyl group, $C_6H_5–CH_2–$)
M−92 (loss of a pyridylmethyl group, $C_6H_5N–CH_2–$)
M−105 (loss of a benzoyl group, $C_6H_5C(=O)–$)
M−119 (loss of a methylbenzoyl group, $CH_3C_6H_4C(=O)–$)
M−127 (loss of an iodide atom, I)

Number of Carbon Atoms

The number of C atoms can be calculated from the relative intensities of the molecular ion peak, M and the isotope peak M + 1, which is one mass above the molecular ion. In addition, the natural abundance of ^{13}C isotope, which is 1.11%, is to be taken into consideration. Thus, the number of C atoms = [(M + 1)/M]/0.011. For example, in the mass spectrum of naphthalene, the molecular ion at mass 128 has a relative intensity of 100 while the peak at 129 has an intensity of 11. The number of C atoms in the compound, therefore, is (11/100)/0.011 or 10. Another way of calculating the number of C atoms, especially where the molecular ion is also the most intense peak, such as that in benzene or acetylene, is by applying what is known as the "rule of 13." That is, the number of C atoms = mass of molecular ion/13. For instance, in the mass spectra of acetylene, the molecular ion 26 is the most intense peak. The number of C atoms, therefore, in acetylene is 26/13 or 2. Since two carbon atoms will account for the mass 12 × 2 or 24 the number of hydrogen atoms, therefore, is 26 − 24 or 2. The molecular formula for acetylene as determined here from such calculation is correctly C_2H_2. Similarly, we can calculate the molecular formulas for benzene or naphthalene in the same manner. In naphthalene, the number of C atoms calculated above is 10, thus accounting for a mass of 12 × 10 or 120. The number of hydrogen atoms in this compound is therefore 128 − 120 or 8, corresponding to a molecular formula $C_{10}H_8$.

Nitrogen Rule

When an organic molecule contains N atom(s), its fragmentation pattern under electron impact ionization may be interpreted with some degree of accuracy by the nitrogen rule. When the molecular ion, M^+ is of odd mass, containing an odd number of N atom(s), the fragmented ions of high abundances will have masses with *m/z* of even numbers. For instance, when the molecular ion has a mass of the odd number 87 for $(C_2H_5)_2N^{\bullet+}CH_3$, the two most abundant ions have the even masses of 72 and 44, respectively, corresponding to the fragmented ions $CH_2{=}N^+(C_2H_5)(CH_3)$ and $H_2C{=}N^+H(CH_3)$, respectively. When the molecular ion M^+ has an even mass and contains an even number of N atom(s) the major fragmented ions in the mass spectra will have odd *m/z*.

Index of Hydrogen Deficiency

The IHD is used to calculate the number of rings and double bonds. For a compound with molecular formula $C_xH_yN_zO_n$, IHD = $x-(y/2) + (z/2) + 1$, where x, y, and z are the number of C, H, and N atoms in the molecular formula, respectively.

Determination of Molecular Formula

The molecular formula of an unknown substance in certain cases may be determined from careful interpretation of its mass spectra. Some information, however, must be known to do such interpretation. First and foremost, the mass spectra must show a clear and distinct from any stray background masses, and also one should be able to measure the abundance of such molecular ion. Sometimes, the presence of contaminants and often peaks arising from column bleed can make this task difficult. In addition, some general ideas about the types or the nature of the compounds expected to be found in the sample is always helpful. The following are some general guidelines and helpful hints for interpreting a mass spectrum.

To begin with, identify the molecular ion, the peak (if it appears in the mass spectrum) seen at the highest *m/z* in the mass spectrum except for the isotope peaks, such as $[M + 1]^+$ or $[M + 2]^+$. Then, look for the mass ions $[M + 1]^+$ (^{13}C, ^{15}N) and $[M + 2]^+$ (^{18}O, ^{34}S, ^{37}Cl, ^{81}Br). Assume the molecular formula as $C_xH_yN_zO_n$ and try to calculate its probable formula. Make a note whether the nominal mass is even or odd and apply the "nitrogen rule." Nominal mass is the mass of the most abundant

natural isotope expressed as the nearest integer. Now look for the low mass ions (the primary and secondary ions) resulting from fragmentation. Compile all the information including fragmentation to establish the structure.

The total number of C atoms present in the compound can be determined from the relative intensities of the molecular ion M^+ and $[M + 1]^+$ and using the natural abundance 1.11% for ^{13}C isotope as shown above. Then, apply the "rule of 13" to derive the base formula assuming that the compound contains only C and H atoms. If oxygen is present, substitute one CH_4 unit from the base formula with an O atom, since the mass of O is equal to that of CH_4, which is 16. Now for nitrogen, if it is known or expected to be present in the compound remove one CH_2 unit from the base formula and substitute with an N atom, both of which have the same mass 14. The number of double bonds and rings in the compound $C_xH_yN_zO_n$ may be determined from the IHD using the formula, $x–(y/2) + (z/2) + 1$. This is illustrated below for 4-hydroxyphenylacetamide as an example. The compound contains the elements C, H, O, and N and several double bonds.

The mass spectra of this compound show the presence of the molecular ion at *m/z* 151 having a relative intensity of 44% in comparison to that of the base peak at mass 109. The $[M + 1]^+$ ion at *m/z* 152 shows a relative intensity of 4%. The first step now is to determine the number of C atoms in the compound as shown above. Thus, the number of C atoms = (4/44)/0.011 or 8 (taking only the whole number ratio). Next, apply the "carbon-13 rule" to determine the base formula, that is, the molecular formula that contains only C and H atoms. This is done by dividing the mass of the molecular ion with 13 and taking only the whole number integer value for the C atoms in the base formula. Thus, the number of carbon atoms in the base formula is 151/13 or 11. The 11 C atoms should constitute a total mass of 12 × 11 or 132 of the molecular mass 151. The number of H atoms in the base formula therefore is (151−132) or 19. Thus the base formula of this compound is $C_{11}H_{19}$. The odd mass may infer the presence of an odd number of N atom(s). Thus, adding one N atom to this base formula and subtracting a $–CH_2$ unit for compensating to retain the same molecular mass 151 should now give us a formula $C_{10}H_{17}N$. We can proceed in the same way for O atoms, that is, substituting one O atom in $C_{10}H_{17}N$ for a $–CH_4$ should give a formula $C_9H_{13}NO$ while substituting two O atoms should give a formula $C_8H_9NO_2$. Since the total number of C atoms as calculated above is 8 and not 9, the compound, therefore, should have the formula $C_8H_9NO_2$ and not $C_9H_{13}NO$. The total number of the double bonds and cycle (ring) in the structure may now be calculated from the IHD. The IHD in this case should be (8 − 9/2 + 1/2 + 1) or 5. From all this information and looking at the mass of the fragmented base ion the structure of the compound may be assigned as HO–phenyl–NH–CCH_3(=O). The loss of a –C(=O)–CH_3 fragment from the above structure should yield the fragment ion [HO–phenyl–NH–] with the mass 109. The primary characteristic mass ion in the mass spectrum of the above compound is seen at 109 as expected, thus confirming our proposed structure.

Chemical Ionization

The fragmentations of molecules under electron impact ionization sometimes do not produce the molecular ions in measurable abundance. Such peaks of molecular ions in the mass spectra cannot be then ascertained to determine the molecular masses of substances. However, such a problem may be eliminated by using CI which produces much larger molecular ion peaks. In CI, a stream of reagent gas is injected along with the sample into the source that brings up the source pressure to 0.3–1.0 Torr, which is much higher than the pressure range in the electron impact ionization, 10^{-3}–10^{-5} Torr. Such reagent gases used under CI include methane, ethane, isobutane, ammonia, and water vapor. The electron beam in CI almost exclusively ionizes the reagent molecules that are in much larger numbers over the sample molecules. The excited ions of the reagent gas molecules then undergo ion–molecule reactions with the sample molecules as well as with other reagent molecules. In other words, the extent of fragmentation of sample molecules under CI is much less than that under EI. The sample molecules mostly remain intact showing large molecular ions in the mass

spectra. In CI, electrons with higher energy up to 400 eV are used at the pressure of 1 Torr in comparison to the electron energy of 70 eV used under EI at 10^{-3}–10^{-5} Torr.

In atmospheric pressure chemical ionization (APCI) sources, the CI occurs at much higher pressures. The sample introduction is relatively simple. Such mass selective detectors are usually interfaced to an LC for the determination of molecules of much larger masses. The applications of APCI in environmental analyses are less.

Limitation of GC/MS Analysis

Although GC/MS is the most confirmative technique to identify an analyte, it, however, has some limitations. First, the detection limit is relatively higher for any compound when compared to most other GC or HPLC detectors. Often the detection limits required to meet the regulatory compliances might not be achieved by using MS under low resolution. Such low detection, however, could be attained under the SIM mode where certain selected mass ions of interest, namely, the primary and a few major secondary characteristic ions of the target compounds are only sought for in the ion chromatogram. In addition, the detection levels can be lowered using high-resolution MS. The cost and servicing of such instrument, however, for routine analysis could be expensive.

The isomers of a compound such as *ortho*-, *meta*-, and *para*-xylenes cannot be distinguished from each other as they produce the same characteristic mass ions. Thus, the position of the substituent(s) in the aromatic ring in compounds cannot be ascertained fully from their mass spectra. Similarly, the polynuclear aromatic hydrocarbons, anthracene and phenanthrene with three benzenoid rings in their structures produce the same mass spectra, and therefore, distinguishing such substances (and many of which usually or almost co-elute) may require better resolution and well separation for the identification of their peaks from their retention times. Many types of substances, such as alkanes, fragment under the electron impact ionization producing a series of spectra common to all the compounds of that class. Therefore, such substances cannot be identified individually unless their molecular mass ion peaks are distinctly distinguished over the background levels of noise or column bleed. Their mass spectra, however, may serve as a signature of their classes.

U.S. EPA METHODS

For the analysis of organic pollutants in environmental samples, the U.S. EPA has classified them into two categories: volatile organics and semivolatile organics (Figure 4.1) (U.S. EPA, 1992). The

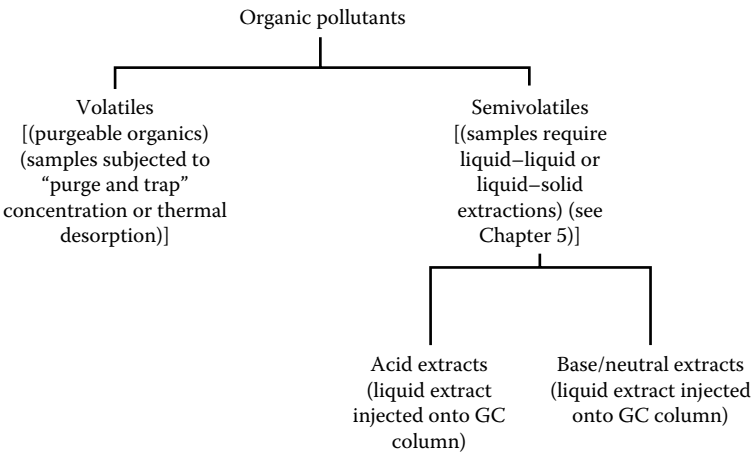

FIGURE 4.1 Classification of organic pollutants based on sample extraction technique.

substances in the former category are those that are more or less volatile at ambient temperature and pressure. This classification, however, is based on the analytical technique used rather than the chemical structures of pollutants. For example, chloroform and *p*-xylene are very different in their structures and chemical properties. The only property that groups them together is that both are volatile substances. Although volatile pollutants are expected to have low boiling points, a few compounds such as ethylbenzene, xylenes, or dichlorobenzenes have boiling points higher than that of water. A full list of volatile organic compounds along with their characteristic mass ions is presented under volatile organic compounds in Chapter 63.

VOLATILE ORGANICS BY PURGE AND TRAP METHOD

Two techniques may be applied to transfer the volatile analytes from the sample matrices onto the GC column: purge and trap technique and thermal desorption. In the purge and trap method, an aliquot of aqueous sample (usually 5 mL for wastewaters and 25 mL for drinking waters) is bubbled through by helium or nitrogen for 11 min. The analytes are purged out from the sample and carried over with the purging gas onto a trap consisting of activated charcoal, tenax, and silica gel adsorbents where they are adsorbed. The trap is then heated at 180°C for 4 min. The analytes are desorbed and transported by the carrier gas onto the GC column.

For soil or solid waste samples, an accurately weighted amount of sample is treated with methanol. A small portion of the methanol extract (usually between 10 and 100 mL, depending on the expected level of analyte concentrations in the sample and the presence of matrix interference substances) is injected into 5 mL of laboratory reagent-grade water taken in the purging vessel that is then purged with an inert gas. Analytes adsorbed over the trap are desorbed by heating and transported to the GC column.

Calculation involving analyte concentration in the solid matrix is shown in the following example.

EXAMPLE 4.1

Two grams of soil was treated with 10 mL methanol. A 100 μL aliquot of methanol extract was injected into 5 mL reagent grade water for purge and trap analysis of a volatile organic compound. The concentration of the analyte was found to be 22 mg/L. Determine its concentration in the soil.

This problem can be solved by either of the following two ways:

1. A mass calculation:

$$22\,\text{mg analyte/L} = 22\,\text{mg} \times 5\,\text{mL water}/1000\,\text{mL water} = 0.11\,\text{mg}$$

That is, 0.11 mg analyte was found to be present in 5 mL of the aqueous solution of the methanol extract in the purging vessel. This amount must have come from 100 μL methanol extract of the soil injected into this 5 mL water in the purging vessel; that is, 0.11 mg analyte/100 μL methanol extract. The mass of the analyte in 10 mL methanol extract and therefore in the starting amount of 2 g soil:

$$= 0.11\,\text{mg analyte} \times 10\,\text{mL (or } 10{,}000\,\mu\text{L})/100\,\mu\text{L} = 11\,\text{mg}$$

In other words, 2 g soil sample contained 11 mg analyte. Therefore, 1 kg or 1000 g soil contained (11 mg × 1000 g/2 g) or 5500 g. That is, the concentration of the analyte in the soil is 5500 mg/kg.

2. The above problem may alternatively be solved as follow by what is known as "dimensional analysis" using a series of conversion factors: (22 mg analyte/1 L water) × (1 L water/1000 mL water) × (5 mL water/100 μL methanol) × (1000 μL methanol/1 mL methanol) × (10 mL methanol/2 g soil) × (1000 g soil/1 kg soil) = 5500 mg analyte/kg soil.

SEMIVOLATILE ORGANICS

Organic substances that are not volatile are grouped under semivolatiles. The latter class also includes substances of very low volatility such as chlorinated biphenyls and polynuclear aromatics. As far as the GC/MS technique goes, the principle of analysis of the semivolatile organics is not so distinctly different from that of the volatile organics. On the other hand, the method of extraction of analytes from the sample matrices and the sample concentration steps for these semivolatile organic compounds vastly differs from that of the volatile organics. Such extraction techniques and the sample cleanup methods are discussed more extensively in Chapter 5. In addition, a full list of semivolatile compounds, their detection limits, and characteristic mass ions are further discussed in Chapter 55.

Tuning

Before beginning any analysis, an instrument must be checked for its performance. Every factory-built GC/MS instrument is equipped with a tuning substance, such as perfluorotributylamine (PFTBA). The characteristic mass ions of this compound (or any other tuning compound) and the relative area response corresponding to these mass ions have been well established and set as guidelines to check the performance of the instrument. This is called tuning. All instruments must meet such tuning criteria to perform general organic analysis satisfactorily. In order to achieve highly reliable and accurate results, the U.S. EPA has mandated the use of additional tuning substances and set the acceptable performance criteria for environmental analysis of organic pollutants by GC/MS. The two tuning substances for volatile and semivolatile organic compounds are 4-bromofluorobenzene (BFB) and decafluorotriphenylphosphine (DFTPP), respectively. Decaflurotriphenylphosphine oxide (DFTPPO) is used as a tuning substance for the LC/MS analysis of certain nitrogen-containing pesticides. The GC/MS system must be checked to see if the acceptable performance criteria are achieved. All the key *m/z* criteria for the BFB and DFTPP tuning are listed in Tables 4.1 and 4.2, respectively.

Inject 2 μL (50 ng) of BFB or DFTPP solution. Alternatively, 2 μL of BFB solution may be added to 5 mL of reagent water and analyzed after purge and trap concentration. A background correction should be made prior to checking the *m/z* criteria of the mass spectra. If the instrument has passed the DFTPP test earlier in the day, it may not be necessary to perform a BFB test for the volatiles when using the same instrument. It is only after the tuning criteria are met that the calibration standard solutions, blanks, and the samples are to be analyzed.

TABLE 4.1
BFB Tuning Requirement for Volatile Organic Analysis

Ion Mass	Abundance Criteria
50	15%–40% of mass 95
75	30%–60% of mass 95
95	Base peak, 100% relative abundance
96	5%–9% of mass 95
173	Less than 2% of mass 174
174	Greater than 50% of mass 95
175	5%–9% of mass 174
176	95%–101% of mass 174
177	5%–9% of mass 176

TABLE 4.2
DFTPP Tuning Requirement for Semivolatile Organic Analysis

Ion Mass	Abundance Criteria
51[a]	30%–60% of mass 198
68	Less than 2% of mass 69
70[b]	Less than 2% of mass 69
127[c]	40%–60% of mass 198
197[d]	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5%–9% of mass 198
275[e]	10%–30% of mass 198
365[f]	Greater than 1% of mass 198
441	Present but less than mass 443
442[g]	Greater than 40% of mass 198
443[h]	17%–23% of mass 442

[a] From 10% to 80% of mass 198 for Method 525 (drinking water).
[b] Must be present for CLP requirement.
[c] From 10% to 80% of mass 198 for Method 525 (drinking water) and 25% to 75% of mass 198 for CLP requirement.
[d] Less than 2% of mass 198 for Method 525 (drinking water).
[e] From 10% to 60% mass 198 for Method 525 (drinking water).
[f] Greater than 0.75% of mass 198 for CLP requirement.
[g] Greater than 50% of mass 198 for Method 525 (drinking water) and from 40% to 100% of mass 198 for CLP requirement.
[h] From 15% to 24% of mass 198 for Method 525 (drinking water) and CLP requirement.

The following instrumental conditions are required for the tuning and analysis:

Electron energy: 70V (nominal)
Mass range: 20–260 amu for volatiles and 35–450 amu for semivolatiles
Scan time: To give at least five scans per peak but not to exceed 7s per scan

For the analysis of semivolatile organics, a column performance test for the base/neutral and the acid fractions must be performed to determine the efficiency of the chromatographic column for separation of the analytes. For the base/neutral fraction, inject 100 ng of benzidine and calculate the benzidine-tailing factor that must be less than 3 . Similarly, for the acid fraction, inject 50 ng of pentachlorophenol and calculate its tailing factor that must be less than 5 . The calculation of the tailing factor is shown in Figure 4.2. Both benzidine and pentachlorophenol may be added onto the DFTPP standard solution and injected. If the column performance test fails, replace the column packing to achieve the tailing factor criteria.

$$\text{Tailing factor} = \frac{\text{EB}}{\text{AE}}$$

$$\text{Peak height, CD} = 100\,\text{mm}$$

$$10\,\text{Peak height, CE} = 10\,\text{mm}$$

$$\text{Peak width AB at } 10\%\,\text{peak height} = 52\,\text{mm}$$

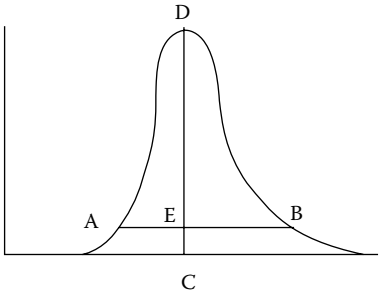

FIGURE 4.2 Tailing factor calculation.

$$\text{AE} = 20\,\text{mm}$$
$$\text{EB} = 32\,\text{mm}$$
$$\text{Tailing factor} = \frac{\text{EB}}{\text{AE}} = \frac{32}{20} = 1.6$$

COMPOUND IDENTIFICATION

The analytes are identified from their mass spectra and retention times. The retention time must fall within ±3 s of the retention time of the known compound. The mass spectra of the unknown peak must have the primary and all secondary characteristic ions (and often the molecular ion).

Calibration

One of the following three methods can perform the quantitation of an analyte:

1. External standard method
2. Internal standard method
3. Isotope dilution method

The first two methods have been discussed earlier under "Gas Chromatography" in Chapter 3. The isotope dilution method, which is not so frequently employed for quantitation because of the cost, is somewhat similar to the internal standard technique and is presented below in brief.

In the isotope dilution method, labeled analogs of analytes are first added onto the standard solutions of the analytes as well as to the samples/sample extracts. Before the analysis, a calibration curve is prepared plotting relative response (RR) against concentrations using a minimum of five data points. RR of a compound is measured from the isotope ratios of the compound and its labeled analog as follows:

$$\text{RR} = \frac{(R_l - R_m)(R_s + 1)}{(R_m - R_s)(R_l + 1)}$$

where

R_s is the isotope ratio in the pure standard
R_l is the isotope ratio in the pure labeled compound
R_m is the isotope ratio in the mixture

$$C_s = \frac{A_s \times C_{is}}{A_{is} \times \text{RF}}$$

Isotope ratio is measured as the ratio of the area of the primary ion of the unlabeled compound to that of the labeled compound. When the area is zero, it is assigned a value of 1. The retention times of the analytes in most cases are the same as that of their labeled analogs. The isotope can be calculated from the extracted ion current profile (EICP) areas. An example of EICP for benzene, benzene-d_6, and a mixture of benzene and benzene-d_6 is presented in Figure 4.3. Calculation to determine the RR is given below:

$$R_l = \frac{1}{74,592} = 0.000134$$

$$R_s = \frac{105,670}{1} = 105,670$$

$$R_m = \frac{m/z78}{m/z84} = \frac{87,445}{69,528} = 1.2577$$

Therefore,

$$\text{RR} = \frac{(0.0000134 - 1.2577)(105,670 + 1)}{(1.2577 - 105,670)(0.0000134 + 1)}$$
$$= 1.2577$$

As mentioned earlier, an appropriate constant amount of the labeled compound is spiked to each of the calibration standards. The RR at each concentration is determined which is then plotted

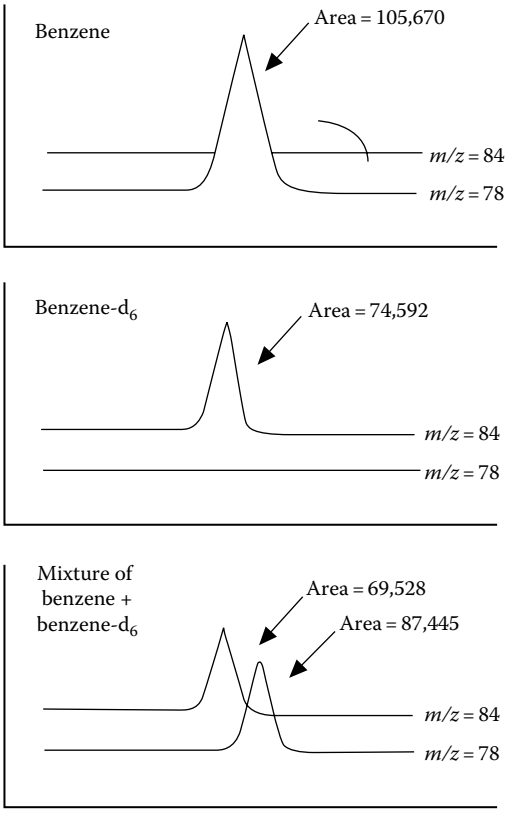

FIGURE 4.3 An example of ECIPs for benzene, benzene-d6, and a mixture of benzene and benzene-d_6.

against the concentration to prepare a calibration curve. The RR of the analytes in the sample (or sample extract) is matched in the linearity range of the calibration curve to determine their concentrations. If the ratio of the RR to concentration is constant (<20% relative standard deviation) over the calibration range, an averaged ratio may alternatively be used instead of the calibration curve for that compound.

It may be noted that for doing such calibration, each analyte is needed to be spiked with its labeled analog. This increases the cost of the analysis. Such high cost and often unavailability of the labeled analogs are the major drawbacks of the isotope dilution method as compared to the external and internal standard calibration methods. However, the isotope dilution method should be more accurate theoretically than the internal standard method, because the chromatographic response and the retention times of the analytes are closest to their corresponding labeled analogs.

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5 Extraction of Organic Pollutants and Sample Cleanup

SAMPLE EXTRACTION

Organic pollutants in potable or nonpotable waters, soils, sediments, sludges, solid wastes, and other matrices must be brought into an appropriate organic solvent for their injection into the GC column. Such extraction also enables the increase of the concentration of analytes in the samples by several orders of magnitude for their detection at ppb or ppt level. Depending on the nature of the sample matrices, various extraction techniques may be effectively applied for the accurate and low-level detection of organics. These are outlined in Figure 5.1.

There are also other analytical techniques, mostly pertaining to miniaturized microextractions developed in recent years. Such methods, however, are not used in routine environmental analysis. They involve using a very small volume of liquid (in the microliter range) in the liquid-phase microextraction (LPME) or a very small amount of solid or semi-solid polymeric material in the solid-phase microextraction (SPME). The LPME techniques use small droplets of organic solvents suspended from the tip of a micro-syringe. Modified LPME methods use porous hollow fibers for protection of the extracting solvent. In SPME, a small diameter fiber coated with a small volume of stationary phase is placed either in the aqueous sample or in the gas sample. The analytes partition into the coated solid fiber and then thermally desorbed out for GC analysis. Several alternate approaches have been introduced. One such modification is the "in-tube" SPME developed essentially for HPLC analysis. The microextraction methods have not been implemented yet in environmental analysis. In-depth studies on the precision, accuracy, and method performance of these techniques are needed to be carried out for their potential applications in environmental analysis.

LIQUID–LIQUID EXTRACTION

Aqueous samples are commonly extracted by liquid–liquid extraction (LLE) technique. A measured volume of the liquid sample is repeatedly extracted with an immiscible organic solvent. The selection of the organic solvent must meet the following criteria:

1. It must be immiscible with water.
2. The organic pollutants should be soluble in the solvent (their solubility must be greater in this solvent than in water).
3. The density of the solvent should be greater than water when the extraction is carried out in a separatory funnel or a continuous liquid–liquid extractor; on the other hand, the solvent should be less dense than water when the microextraction is performed in a glass vial.

Upon mixing the aqueous sample with the solvent, the pollutants dissolve more in the latter because they are more soluble in the solvent. In other words, they partition or distribute in the aqueous and the solvent phases and at equilibrium, the ratio of concentration of the solute in both the phases is constant.

The partition or distribution coefficient, P, is equal to the ratio of the concentration of the solute in the solvent to that in the water, that is,

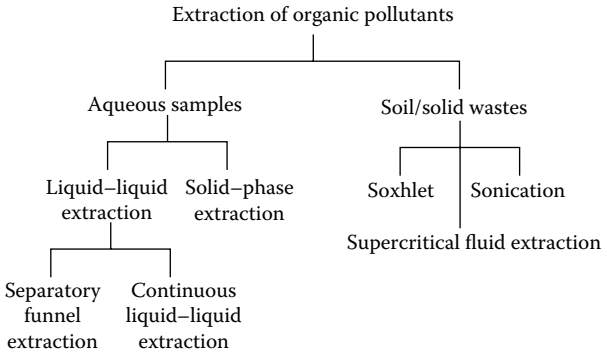

FIGURE 5.1 Schematic diagram of various extraction techniques.

$$P = \frac{C_{\text{solvent}}}{C_{\text{water}}}$$

Since P is independent of volume ratio but constant at any given temperature, increasing the volume of the solvent will cause more dissolution of the solute into the solvent. In other words, the greater the amount of solvent, the more of the solute would dissolve in it. Again, for any given volume of solvent, repeated extractions using smaller portions in equal amounts will give greater extraction efficiency than a single-step extraction. For example, in the extraction of semivolatile organics, high-extraction efficiency is achieved by three successive extractions using 60 mL quantity of methylene chloride each time rather than one single step extraction with 180 mL solvent.

Certain widely used solvents such as diethyl ether or methylene chloride are highly volatile. Excess pressure buildup may cause rupture of the separatory funnel. Many accidents have been reported. It is important to vent out the excess pressure, especially after the first time of shaking the sample with the solvent. Before extraction, rinse the separatory funnel with a few milliliters of the solvent. A glass container that has even a slight crack should not be used for extraction.

Solid Phase Extraction

Organic substances can be extracted from aqueous samples by solid–liquid (known as solid phase) extraction. The process is simple, fast, and cost effective in comparison to LLE. In addition, the analysis can be carried out using a smaller volume of sample. By using a suitable capillary column, a detection level comparable to the LLE-packed column could be readily attained. The method requires a measured volume of the aqueous sample to be passed through a cartridge tube packed with a suitable solid adsorbent material. The organic pollutants in the sample are adsorbed onto the solid surface from which they are eluted by a properly selected solvent. The sample is applied at the top of the tube and drawn through the bed by a syringe or vacuum, maintaining a flow rate of 1–2 drops/s. Alternatively, larger pore size particles may be used to allow fast flow rates for large volume samples. The tube is washed with a nonpolar solvent for polar analytes, and with a polar solvent for nonpolar analytes. Finally, the analytes are eluted out of the column by a suitable solvent. Polar solvents should be used for polar analytes, and nonpolar solvents for nonpolar analytes. The sample extracts may be concentrated further by evaporation of the solvent.

The selection of adsorbent-packing material is based on the polarity of the pollutants to be analyzed. The nonpolar hydrophobic adsorbents retain the nonpolar analytes and allow the polar substances to pass through the column. The hydrophilic adsorbents adsorb the polar components, allowing the nonpolar materials to pass through. Various stationary phases for solid phase extraction are listed in Table 5.1.

TABLE 5.1
Stationary Phases for Solid Phase Extraction

Nonpolar compounds	Octadecyl (C-18) bonded silica, octyl (C-8) bonded silica
Moderately polar compounds	Phenyl-, ethyl-, and cyclohexyl bonded silica
Polar compounds	Silica, Florisil, silica gel, cyano-, diol-, and amino groups bound to silica, silicates, and alumina

Soxhlet Extraction

Solid samples may be conveniently extracted for semivolatile and nonvolatile organic pollutants by Soxhlet extraction. The sample is placed in a porous extraction thimble and immersed in the solvent. The extraction comprises a series of batch processes involving distillation and condensation of the solvent along with periodic fill-in and siphoning of the solvent in and out of the extraction chamber. This causes an intimate mixing of the sample with the solvent. Soxhlet extraction using a fluorocarbon solvent is commonly employed to leach out petroleum hydrocarbons from the soil. Other than this use, its application in environmental analysis is limited, because it is slow, taking up several hours to complete. The extraction also requires a relatively large quantity of solvent and usually a preconcentration step is necessary.

Supercritical Fluid Extraction

A supercritical fluid is defined as a substance that is above its critical temperature and pressure. It exhibits remarkable liquid-like solvent properties and, therefore, high extraction efficiency. Such common gases as carbon dioxide and nitrous oxide have been successfully employed as supercritical fluids in the extraction of organics from solid matrices. The solid sample is placed in an extraction vessel into which the pressurized supercritical fluid is pumped. The organic analytes dissolve in the supercritical fluid and they are swept out of the extraction chamber into a collection vessel. The pressure is released at the valve attached to the collection device where it drops down to atmospheric pressure. The supercritical fluid then returns to its gaseous state and escapes, leaving analytes in the collection vessel in an appropriate solvent such as methylene chloride.

The extraction efficiency of supercritical fluids may be enhanced by mixing into them a small amount of a cosolvent such as acetone or methanol. Supercritical fluid extraction offers certain advantages over other extraction processes: (1) it is a relatively fast process with greater extraction efficiency, (2) sample concentration steps may be eliminated, and (3) unlike LLE or Soxhlet extraction, a large amount of organic solvents is not required.

CLEANUP

Sample extracts injected into the GC can cause loss of detector sensitivity, shorten the lifetime of a column, produce extraneous peaks, and deteriorate peak resolution and column efficiency. The sample extracts may be purified by one or more of the following techniques:

1. Partitioning between immiscible solvents
2. Adsorption chromatography
3. Gel permeation chromatography
4. Destruction of interfering substances with acids, alkalies, and oxidizing agents
5. Distillation

The cleanup procedures presented in Table 5.2 may be applied for different classes of organic substances.

TABLE 5.2
Cleanup Methods for Organic Extracts

Analyte Group	Cleanup Method(s)
Priority pollutants (semivolatiles)	GPC, acid–base, sulfur
Organochlorine pesticides	Florisil, GPC, sulfur
PCBs	Florisil, GPC, sulfur, $KMnO_4$–H_2SO_4
Organophosphorus pesticides	Florisil, GPC
Chlorinated herbicides	Acid–base
Chlorinated hydrocarbons	Florisil, GPC
Polynuclear aromatic hydrocarbons	Alumina, silica gel, GPC
Nitroaromatics	Florisil, GPC
Cyclic ketones	Florisil, GPC
Nitrosamines	Alumina, Florisil, GPC
Phenols	GPC, acid–base, silica gel (on derivatized phenols)
Phthalate esters	Alumina, Florisil, GPC
Petroleum waste	Alumina, acid–base

Note: GPC, gel permeation chromatography.

Acid–Base Partitioning

This is applied to separate acidic or basic organics from neutral organics. The solvent extract is shaken with water that is highly basic. The acidic organics partition into the aqueous layer whereas, the basic and neutral compounds stay in the organic solvent and separate out. After this, the aqueous layer is acidified to a pH below 2, and then extracted with methylene chloride. The organic layer now contains the acid fraction. Phenols, chlorophenoxy acid, herbicides, and semivolatile organic pollutants are cleaned up by the procedure described above.

Alumina Column Cleanup

Highly porous and granular aluminum oxide (available in three pH ranges: acidic, neutral, and basic) is used in column chromatography. Analytes are separated from the interfering compounds by virtue of their different chemical polarity.

The column is packed with alumina, and then covered under anhydrous Na_2SO_4. The extract is then loaded on it. A suitable solvent is selected to elute the analytes. The interfering compound is left adsorbed onto the column. The eluate is then concentrated further. Alumina can be prepared in various activity grades by adding water to grade I (prepared by heating at $>400°C$ until no more water is lost). Among the common pollutants, phthalate esters and nitrosamines are separated. Basic alumina (pH 9–10) is most active in separating basic and neutral compounds: alkalies, alkaloids, steroids, alcohols, and pigments. Certain solvents such as acetone or ethyl acetate cannot be used. This form of alumina can cause polymerization, dehydration, and condensation reactions.

The neutral form is less active than the basic grade and is used to separate aldehydes, ketones, esters, lactones, etc. Acidic form (pH 4–5) is used to separate strong acids and acidic pigments. Alumina column cleanup is also used to separate petroleum wastes.

Silica Gel Cleanup

Silica gel is a form of amorphous silica with weak acidic properties. It is made by treating H_2SO_4 with sodium silicate when used for cleanup purposes. Interfering compounds of different polarity

are absorbed onto and retained on the column. There are two types of silica gel: activated and deactivated. The former is prepared by heating silica gel for several hours at 150°C. It is used to separate hydrocarbons. The deactivated form contains 10%–20% water and it is used to separate plasticizers, steroids, terpenoids, alkaloids, glycosides, dyes, lipids, sugar, esters, and alkali metal cations. In environmental analysis, silica gel is used to cleanup sample extracts containing single component pesticides, PCBs, polynuclear aromatic hydrocarbons, and derivatized phenolic compounds. Methanol and ethanol decrease adsorbent activity.

Florisil Column Cleanup

Florisil is a form of magnesium silicate with acidic properties. It is used for the cleanup of sample extracts containing the following types of analytes: organochlorine pesticides, organophosphorus pesticides, phthalate esters, nitrosamines, haloethers, nitroaromatics, and chlorinated hydrocarbons. Florisil is also used to separate aromatic compounds from aliphatic–aromatic mixtures, as well as to separate esters, ketones, glycerides, steroids, alkaloids, and some carbohydrates. It also separates out nitrogen compounds from hydrocarbons.

The column is packed with Florisil, topped with anhydrous sodium sulfate, and then loaded with the sample to be analyzed. Suitable solvent(s) are passed through the column. The eluate is concentrated for analysis, while the interfering compounds are retained on the column.

Gel-Permeation Cleanup

This separation is based on the size of porous hydrophobic gels. The pore size must be greater than the pore size of the molecules to be separated. Gel-permeation cleanup (GPC) is used for cleaning sample extracts from synthetic macromolecules, polymers, proteins, lipids, steroids, viruses, natural resins, and other high molecular weight compounds. Methylene chloride is used as the solvent for separation. A 5 mL aliquot of the extract is loaded onto the GPC column. Elution is carried out using a suitable solvent, and the eluate is concentrated for analysis.

Sulfur Cleanup

Sulfur is found in many industrial wastes, marine algae, and sediment samples. Sulfur may mask the region of chromatogram, overlapping with peaks of interest. For example, in the analysis of pesticides, sulfur can mask over many pesticides such as lindane, aldrin, and heptachlor. Sulfur has a solubility that is similar to organochlorine and organophosphorus pesticides and it cannot be separated by the Florisil cleanup method.

The removal of sulfur is achieved by treating the extract with one of the following three substances: copper, mercury, or tetrabutyl ammonium–sodium sulfite reagent.

The sample extract is vigorously shaken with one of the above reagents. The clean extract, free from sulfur, is then separated from the reagent.

Permanganate–Sulfuric Acid Cleanup

Interfering substances in the sample extract may often be destroyed by treating the extract with a strong oxidizing agent, such as $KMnO_4$, or a strong acid like concentrated H_2SO_4, or a combination of both. In such a case, the analyte should be chemically stable to these reagents. For example, interfering substances in the sample extract for the analysis of PCBs can be effectively destroyed by treatment with a small quantity of $KMnO_4$–H_2SO_4 mixture. PCBs are chemically stable under the condition of treatment, and do not react with the acid–permanganate mixture at such a short contact time.

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6 Titrimetric Analysis

Titration is one of the most commonly employed techniques in wet analysis. Many routine analyses of wastewaters, potable waters, and aqueous extracts of sludges and soils can be effectively performed using various titrimetric techniques.

In general, any titrimetric procedure involves the slow addition of a solution of accurately known concentration (a standard solution) to a solution of unknown concentration (sample to be analyzed) until the reaction between both the solutions is complete. In other words, the standard titrant is added slowly up to the point known as the *end point* at which the solute analyte in the sample is completely consumed by the solute in the standard solution. The completion of the reaction is usually monitored by using an indicator that causes a color change at the end point.

Titrimetric methods generally employed in environmental analysis may be broadly classified into the following types:

1. Acid–base titration
2. General redox titration
3. Iodometric titration
4. Argentometric titration
5. Complexometric titration

The above classification highlights the common analytical methods. There is, however, a great deal of overlapping as far as the chemistry of the process is involved. For example, the iodometric method involves an oxidation–reduction reaction between the thiosulfate anion and iodine. However, it is classified here under a separate heading because of its wide application in environmental analysis.

Table 6.1 highlights some of the aggregate properties and parameters that can be determined by various titrimetric methods.

ACID–BASE TITRATION

Acid–base titration involves a neutralization reaction between an acid and a soluble base. The reactants may be a strong acid and a strong base, a strong acid and a weak base, a weak acid and a strong base, or a weak acid and weak base, resulting in the formation of a soluble salt and water. This is shown below in the following examples:

$$HCl(aq) + NaOH(aq) \Rightarrow NaCl(aq) + H_2O(l) \tag{6.1}$$

$$H_2SO_4(aq) + Na_2CO_3(aq) \Rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g) \tag{6.2}$$

In acid–base neutralization reactions, no change occurs in the oxidation number of the metal cation. In the above reactions, for example, there is no change in the oxidation number of sodium that remains in +1 oxidation state, in both the reactant and the product.

One of the most common acid–base indicators is phenolphthalein. In an aqueous solution of pH less than 8, it is colorless. As the pH approaches 10, the color turns red. Some of the common acid–base indicators are listed in Table 6.2. An acid–base titration may be graphically represented by a titration curve, which is a plot between the change of pH versus the volume of acid or base added,

TABLE 6.1
Titrimetric Procedures Applied in Environmental Analysis

Titrimetric Methods	Aggregate Properties/Individual Parameters That Can Be Tested
Acid–base	Acidity, alkalinity, CO_2, ammonia, and salinity
Iodometric	Chlorine (residual), chlorine dioxide, hypochlorite, chloramine, oxygen (dissolved), sulfide, and sulfite
Oxidation–reduction (other than iodometric)	Specific oxidation states of metals, ferrocyanide, permanganate, oxalic acid, organic peroxides, and chemical oxygen demand
Complexometric (EDTA type)	Hardness, most metals
Argentometric	Chloride, cyanide, and thiocyanate

TABLE 6.2
Some Common Acid–Base Indicators

Indicators	Transition Range pH[a]	Color Change
Crystal violet	0.0–1.8	Yellow to blue
Methyl green	0.2–1.8	Yellow to blue
Quinaldine red	1.0–2.2	Colorless to red
Thymol blue	1.2–2.8	Red to yellow
	8.0–9.6	Yellow to blue
Benzopurpirine 48	2.2–4.2	Violet to red
Methyl yellow	2.9–4.0	Red to orange
Congo red	3.0–5.0	Blue to red
Methyl orange	3.2–4.4	Red to yellow
Resazurin	3.8–6.4	Orange to violet
Bromocresol purple	5.2–6.8	Yellow to purple
Phenol red	6.6–8.0	Yellow to red
Cresol purple	7.6–9.2	Yellow to purple
m-Nitrophenol	6.8–8.6	Colorless to yellow
Phenolphthalein	8.3–10.0	Colorless to red[b]
Thymolphthalein	9.4–10.6	Colorless to blue
Alizarin yellow R	10.1–12.0	Yellow to red
2,4,-6-Trinitrotoluene	11.5–13.0	Colorless to orange
Clayton yellow	12.2–13.0	Yellow to amber

[a] The pH range at which the indicator produces color change.
[b] Colorless at pH beyond 13.0.

causing such a pH change. Shapes of some of the titration curves are shown in Figures 6.1 through 6.3. Figure 6.1 illustrates the shape of a titration curve for a strong acid and strong base using the same concentrations of acid and base. Such a titration curve would have a long vertical section, typifying a strong acid–strong base titration. Near this vertical section, the addition of a very small amount of titrant causes a very rapid change in the pH. The midpoint of this vertical section is known as the *equivalence point*, which theoretically should be equal to the end point of the titration. The equivalence point in an acid–base titration involving equal concentrations of a strong acid and a strong base is 7. In other words, a strong acid would completely neutralize an equal volume of strong base of the same strength, or vice versa at pH 7. Figures 6.2 and 6.3 show the titration curves for acids and bases of different strengths. The vertical section is very short in the weak acid–weak base curve.

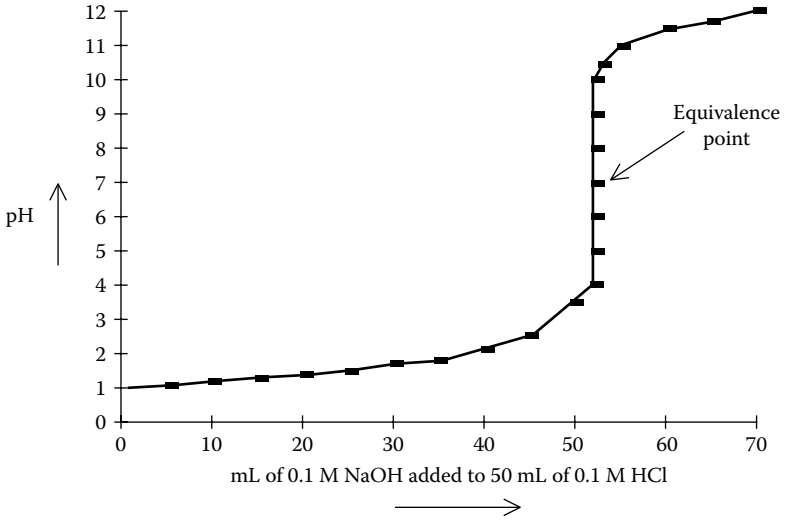


FIGURE 6.1 Titration curve for strong acid and strong base. Indicator producing color change in pH range 4–10 may be used.

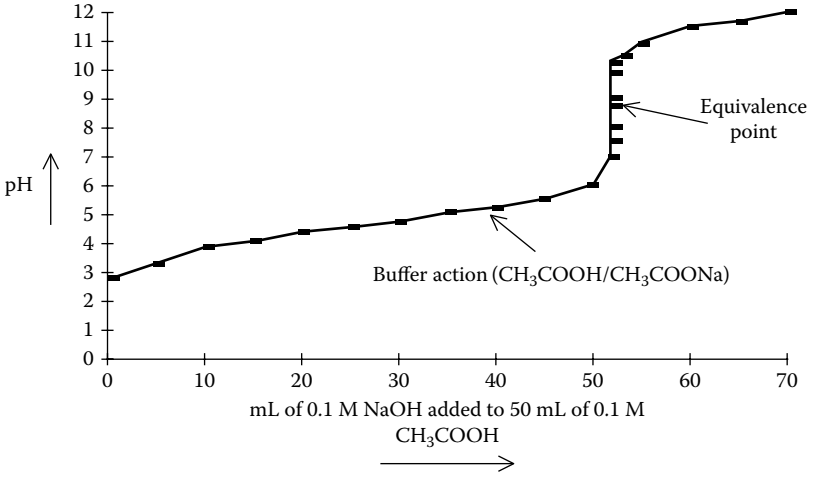


FIGURE 6.2 Titration curve for weak acid and strong base. Indicator producing color change in pH range 7–10 may be used.

The end point in an acid–base titration can be determined either by an acid–base indicator or by means of a potentiometer (or a pH meter). An acid–base indicator is a weak organic acid or a weak organic base that can be written as HY or YOH, respectively, where Y is the complex organic group. In dilute aqueous solution, the indicator, say HY would dissociate as follows:

$$\underset{\text{color-1}}{HY} + H_2O \Leftrightarrow H_3O^+ + \underset{\text{color-2}}{Y^-}$$

In the above example, HY is a weak organic acid and Y^- is the anion or the conjugate base of this acid. HY and Y^- must have different colors. The addition of an acid or base would shift the equilibrium to left or right, respectively, in the above reaction, thus producing more of HY or Y^-.

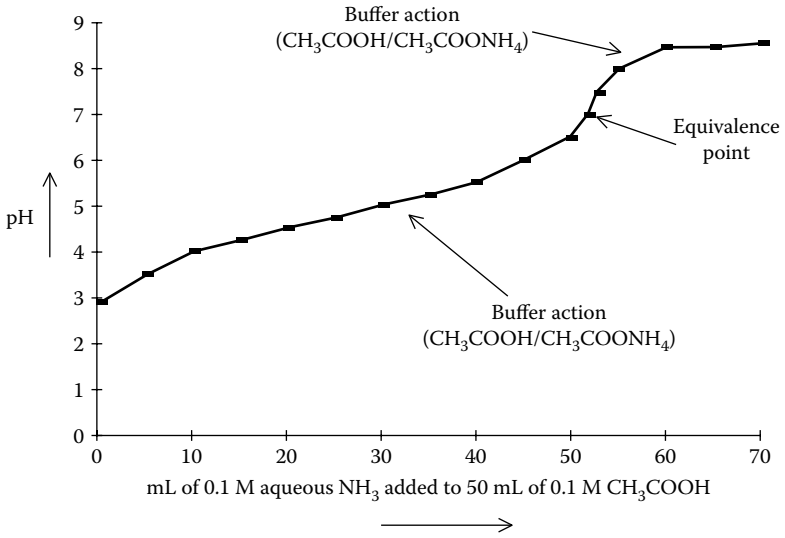


FIGURE 6.3 Titration curve for weak acid and weak base. No color indicator can be used.

Generally, a concentration of Y^- that is 10 times greater than HY should produce the color of Y^- (color-2). Similarly, a HY concentration 10 times over Y^- should produce the color of HY. Selection of an indicator in acid–base titration can be made from looking at the titration curves. Any indicator that produces a color change at a pH range within the vertical section of the titration curve may be employed in the titration. For example, in a strong acid–strong base titration, indicators such as methyl red, methyl orange, phenolphthalein, or bromthymol blue that produce a color change in the pH range 5–10 may be used.

Calculation

The strength of an acid or a base may be determined by either the normality method or by mole calculation as shown below. When normality of one of the reactants is known, the strength of the other reactant can be determined from the following relationship:

$$\text{Volume of acid} \times \text{its normality} = \text{Volume of base} \times \text{its normality}$$

Therefore, the normality of acid

$$= \frac{\text{mL titrant (base)} \times \text{the normality of the titrant (base)}}{\text{mL acid of unknown strength taken in titration}}$$

Similarly, the normality of the base

$$= \frac{\text{mL acid titrant} \times \text{its normality}}{\text{mL base taken in titration}}$$

Normality of a solution is the number of gram equivalents (equivalent weight expressed in grams) of a substance in 1 L of solution or the number of milliequivalent (equivalent weight expressed in milligrams) in 1 mL of solution. Although equivalent weight of a substance may vary according

to the reaction, in most cases, especially, in acid–base titrations where neutralizations completely occur, it may be calculated as follows:

$$\text{Equivalent weight of acid} = \frac{\text{Formula weight}}{\text{Number of replaceable (dissociable) hydrogen atoms}}$$

For example, the equivalent weight of HCl is 36.45/1, or 36.45, H_2SO_4 is 98/2 or 49, or CH_3COOH is 60/1 or 60. In acetic acid, CH_3COOH, although there are totally 5 H atoms, the acid has only one dissociable H atom that ionizes in water as follows:

$$CH_3COOH + H_2O \Rightarrow CH_3COO^- + H_3O^+$$

Similarly, the equivalent weight of a base can be determined by dividing its formula weight by the number of –OH group in its formula unit. For example, equivalent weight of NaOH is 40/1 or 40 and $Ca(OH)_2$ is 74/2 or 37. Many basic substances such as sodium carbonate or sodium bicarbonate do not contain any hydroxyl group. Gram equivalents of these bases are the amounts of these substances that would react with 1 g equivalent of an acid. For example, the equivalent weights of sodium carbonate and sodium bicarbonate may simply be determined from the following reactions:

$$Na_2CO_3 + 2HCl \Rightarrow 2NaCl + CO_2 + H_2O$$
$$NaHCO_3 + HCl \Rightarrow NaCl + CO_2 + H_2O$$

In the above equations, 0.5 mol Na_2CO_3 and 1 mol $NaHCO_3$ react with 1 mol (or 1 g equivalent) of HCl, respectively. Therefore, the equivalent weight of Na_2CO_3 is one-half its formula weight, which is 0.5×106 or 53, and that of $NaHCO_3$ is the same as its formula weight, 84.

The strength or normality of an acid titrant prior to its use in the titration is determined by standardizing against a base such as sodium carbonate of known strength. Other primary standards for acid are *tris*(hydroxymethyl)aminomethane and sodium tetraborate decahydrate. Similarly, a base titrant is standardized against potassium hydrogen phthalate or potassium hydrogen iodate. The following example illustrates the normality-based calculation to determine the strength of an acid or base from a titration experiment.

EXAMPLE 6.1

23.5 mL of 0.025 N NaOH was required to titrate 20 mL of HCl. Determine the strength (normality) of the HCl solution.

$$\text{Normality of HCl} = \frac{23.5\ \text{mL} \times 0.025\ \text{N}}{20.0\ \text{mL}}$$
$$= 0.029$$

Sometimes, it may be more convenient to express the strength of an unknown acid or base in terms of molarity rather than normality. The titrimetric method remains the same. The calculation, however, is based on the molar ratios of reactants in the balanced equation, as cited below in the following two examples.

EXAMPLE 6.2

56.8 mL of 0.01 M KOH was required to titrate 40 mL of a dilute H_2SO_4 solution. Determine the molarity of the acid solution.

$$2KOH + H_2SO_4 \Rightarrow K_2SO_4 + 2H_2O$$
$$2\,mol \quad 1mol \quad 1mol \quad 2\,mol$$

$$\text{Since molarity (M)} = \frac{\text{mol}}{\text{L}} \text{ or } \frac{\text{mmol}}{\text{mL}}\text{, therefore, 56.8 mL of 0.001 M KOH}$$
$$\equiv (56.8 \times 0.01) \text{ or } 0.568 \text{ mmol KOH.}$$

In the above reaction, the molar ratio of KOH to H_2SO_4 is 2:1. Therefore, 0.568 mmol KOH would require 0.568/2 or 0.284 mmol of H_2SO_4.

The volume of H_2SO_4 taken in the titration was 40 mL. Therefore, the strength of the acid = (0.284 mmol/40 mL) + 0.0071 M.

EXAMPLE 6.3

0.2872 g anhydrous Na_2CO_3 was dissolved in water and the volume was made up to 250 mL. 25 mL of this solution was required to titrate 11.2 mL of H_3PO_4. Determine the molarity of the acid. The balanced equation is as follows:

$$3Na_2CO_3 + 2H_3PO_4 \Rightarrow 2Na_3PO_4 + 3H_2O + 3CO_2$$
$$3\,mol \quad 2\,mol \quad 2\,mol \quad 3\,mol \quad 3\,mol$$

$$0.2873\,g\,Na_2CO_3 \text{ is equal to } 0.2873\,g \times \frac{1\,mol\,Na_2CO_3}{106\,g\,Na_2CO_3} \text{ or } 0.00271\,mol\,Na_2CO_3.$$

$$0.00271\,mol\,Na_2CO_3 \text{ would react with } 0.00271\,mol\,Na_2CO_3 \times \frac{2\,mol\,H_3PO_4}{3\,mol\,Na_2CO_3}$$

$$\text{or } 0.00181\,mol\,H_3PO_4 \text{ or } 1.81\,mmol\,H_3PO_4.$$

Therefore, the molarity of phosphoric acid, H_3PO_4 = (1.81 mmol/11.2 mL) = 0.16 M.

OXIDATION–REDUCTION TITRATIONS

An oxidation–reduction titration or redox titration is an oxidation–reduction reaction involving a transfer of electron(s) between two substances in solution. A substance is said to be oxidized when it loses electron(s) and reduced when it gains electron(s). Examples of oxidation–reduction reactions are illustrated below:

$$Ce^{4+} + Fe^{2+} \Leftrightarrow Ce^{3+} + Fe^{3+}$$
$$H_3AsO_3 + 2Ce^{4+} + H_2O \Leftrightarrow H_3AsO_4 + 2Ce^{3+} + 2H^+$$

In the first reaction, Ce^{4+} is reduced to Ce^{3+}, while Fe^{2+} is oxidized to Fe^{3+}. In the second reaction shown above, Ce^{4+} oxidizes arsenous acid to arsenic acid. The oxidation state of As changes from +3 in the reactant, H_3AsO_3, to +5 in the product, H_3AsO_4, while Ce^{4+} is reduced to Ce^{3+}. Ionic reactions like molecular reactions must be balanced. The net charge on the reactants must be equal to that of the products.

Redox titrations find numerous applications in environmental analysis. Iodometric titration involving the reaction of iodine with a reducing agent such as thiosulfate or phenylarsine oxide

TABLE 6.3
Common Oxidizing Agents for Redox Titrations

Oxidant	Standard Potential (V)	Indicator
Potassium permanganate ($KMnO_4$)	1.51	None or terrain
Cerium (IV)[a] (Ce^{4+})	1.44	Ferroin
Potassium bromate ($KBrO_3$)	1.42	α-Naphthoflavone
Potassium iodate (KIO_3)	1.42	α-Naphthoflavone
Potassium dichromate ($K_2Cr_2O_7$)	1.33	Diphenylamine sulfonic acid
Iodine (I_2)	0.536	Starch

[a] Cerium ammonium nitrate, $Ce(NO_3J_4) \cdot 2NH_4NO_3$; cerium ammonium sulfate, $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$; or cerium (IV) hydroxide, $Ce(OH)_4$ may be used to prepare the Ce^{4+} standard solution.

(PAO) of known strength is a typical example of a redox titration. This method is discussed separately in the next section. Another example of redox titration is the determination of sulfite (SO_3^{2-}) using ferric ammonium sulfate, $[NH_4Fe(SO_4)_2]$.

Some common oxidants used as standard solutions in redox titrations are listed in Table 6.3. Potassium permanganate is a strong oxidizing agent that has a standard potential greater than other common oxidants. Its solution has a distinct purple color. One drop of 0.01 M $KMnO_4$ can impart color to 250 mL water. No indicator, therefore, is required in permanganate titration. The end point color, however, fades gradually within 30 s. For dilute permanganate solution, a sharper end point may be obtained by using ferroin (or its derivatives) or diphenylamine sulfonic acid indicator.

The half-reaction for $KMnO_4$ is given below:

$$MnO_4^- + 8H^+ + 5e^- \Leftrightarrow Mn^2 + 4H_2O$$

where Mn is reduced from +7 to +2 oxidation state. The standard potential for this reaction is 1.51 V.

Aqueous solutions of permanganate are not so stable because MnO_4^- can form MnO_2 by reacting with water over time. Therefore, $KMnO_4$ solution needs to be standardized periodically, filtering out any MnO_2 formed, before standardization.

Cerium(IV) solution in 0.1 M H_2SO_4 is an ideal oxidant for many redox titrations. The half-reaction is as follows:

$$Ce^{4+} + e^- \overset{(acid)}{\Leftrightarrow} Ce^{3+} \quad E^o = 1.44\,V$$

The solution is remarkably stable, even at high temperatures. However, it has to be strongly acidic to prevent the precipitation of basic cerium salts.

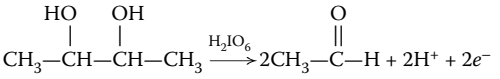
Potassium dichromate is another common oxidizing reagent employed in redox titrations. The titration is carried out in the presence of 1 M HCl or H_2SO_4. The half-reaction is as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \Leftrightarrow 2Cr^{3+} + 7H_2O \quad E^\circ = 1.33$$

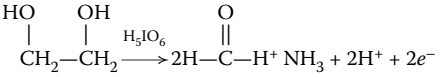
The orange dichromate ion is reduced to green Cr(III) ion; the oxidation state of Cr changes from +6 to +3. The electrode potential of the reaction is lower than those of permanganate and Ce(IV).

The dichromate reactions are relatively slow with many reducing agents. However, dichromate solutions are highly stable and can be boiled without decomposition. Diphenylamine sulfonic acid is commonly used as the indicator in dichromate titration. The indicator is colorless in reduced form and red–violet in oxidized form. Therefore, in a direct titration, the color changes from green (due to Cr^{3+}) to violet.

Periodic acid is another important oxidant. It can selectively oxidize many organic compounds. Compounds containing aldehyde, ketone, or alcoholic groups on adjacent carbon atoms are rapidly oxidized. Similarly, hydroxylamines are oxidized to aldehydes. Some of the half-reactions are shown below:



(Butylene glycol)



(Ethanolamine)

The oxidation state of iodine in periodic acid is +7. In the presence of strong acid, it is reduced to iodate ion. The half-reaction is as follows:

$$H_5IO_+ + H^+ + 2e^- \Rightarrow IO_3^- + 3H_2O \quad E^\circ = 1.6\,V$$

Sodium or potassium salt of periodic acid can be used as a primary standard to prepare periodate solutions.

The application of potassium bromate as an oxidant in direct titration is very little. However, it is used as a source of bromine for many bromination reactions in organic analysis. The analyte solution is acidified. An unmeasured quantity of KBr in excess is added onto it, followed by the addition of a measured volume of standard $KBrO_3$ solution. One mole BrO_3^- generates 3 mol stoichiometric quantity of bromine. The reaction is as follows:

$$BrO_3^- + 5Br^- + 6H^+ \Rightarrow 3Br_2 + 3H_2O$$

After the addition of bromate standard, let the reaction vessel stand for some time to allow the bromination to go to completion. The excess bromine is measured by adding excess KI and titrating the liberated iodine against a standard solution of sodium thiosulfate using starch indicator.

$$KI \Rightarrow K^+ + I^-$$

$$2I^- + Br_2 \Rightarrow I_2 + 2Br^-$$

Many other powerful oxidants are used in redox titrations. Often a metal ion may be present in more than one oxidation state, which must be oxidized or reduced into the desired oxidation state. For example, a salt solution of iron may contain both Fe^{2+} and Fe^{3+} ions. Peroxydisulfates,

bismuthates, and peroxides are often used as auxiliary oxidizing reagents to convert the ion of interest into the higher oxidation state. The half-reactions for these oxidants are as follows:

$$S_2O_8^{2-} + 2e^- \Leftrightarrow 2SO_4^{2-} \quad E^\circ = 2.01\,V$$

(Peroxydisulfate)

Ammonium peroxydisulfate in the acidic medium can oxidize Mn^{2+} to permanganate, Ce^{3+} to Ce^{4+}, and Cr^{3+} to Cr^{6+} (dichromate). The half-reaction for hydrogen peroxide in acid medium is as follows:

$$H_2O_2 + 2H^+ + 2e^- \Leftrightarrow 2H_2O \quad E^o = 1.78\,V$$

The bismuthate ion is reduced to BiO^+ in acid medium, the half-reaction being

$$NaBiO_3 + 4H^+ + 2e^- \Leftrightarrow BiO^+ + Na^+ 2H_2O$$

Standardization of Oxidants

Oxidizing reagents such as tetravalent cerium or potassium permanganate solutions may be standardized by oxalic acid, sodium oxalate, or potassium iodide. The reactions of Ce^{4+} and permanganate ions with oxalic acid in acid medium are given below:

$$2Ce^{4+} + H_2C_2O_4 \Leftrightarrow 2Ce^{3+} + 2H^+ + 2CO_2$$

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \Leftrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Sodium oxalate in acid medium is converted to undissociated oxalic acid, thus undergoing the same reactions as shown above. Ce^{4+} is standardized against oxalic acid or sodium oxalate in HCl solution at 50°C in the presence of iodine monochloride as a catalyst. Permanganate titration is carried out at elevated temperatures (above 60°C). The reaction is initially slow. The Mn^{2+} produced causes autocatalysis. Thus, during the addition of the first few mL of permanganate solution, the violet color persists for a while, but later on, as the reduction progresses with the generation of Mn^{2+}, the permanganate color decolorizes more rapidly. At the end point, the solution turns pink, which persists for about 30 s.

EXAMPLE 6.4

A solution of potassium permanganate was standardized against sodium oxalate ($Na_2C_2O_4$) primary standard. A 50.0 mL 0.01 Ai$Na_2C_2O_4$ standard solution required 37.8 mL $KMnO_4$ solution. Determine the strength (molarity) of $KMnO_4$ solution.

$$\text{Amount of } Na_2C_2O_4 = 0.05\,L\,Na_2C_2O_4 \times \frac{0.01\,mol\,Na_2C_2O_4}{1L\,Na_2C_2O_4}$$
$$= 0.0005\,mol\,Na_2C_2O_4$$

that would react with an amount of

$$KMnO_4 = 0.0005\,mol\,Na_2C_2O_4 \times \frac{2\,mol\,KMnO_4}{5\,mol\,Na_2C_2O_4}$$
$$= 0.0002\,mol\,KMnO_4$$

Thus, the molarity of $KMnO_4$

$$= \frac{0.0002 \text{ mol } KMnO_4}{0.0378 \text{ L } KMnO_4}$$
$$= 0.0053 \text{ M}$$

Periodic acid or periodate solutions are standardized by adding an excess of potassium iodide and then titrating the liberated iodine against a standard solution of sodium thiosulfate, PAO, or sodium arsenite. One mole of periodate liberates an equimolar amount of iodine as per the following reaction:

$$H_4IO_6 + 2I^- \Rightarrow IO_3^- + I_2 + 2OH^- + H_2O$$

The solution must be maintained as slightly alkaline by adding a buffer such as sodium bicarbonate or borax. This prevents any further reduction of iodate.

Among the other oxidizing agents, potassium dichromate and potassium bromate may be used as primary standards without any standardization. The solids should be dried at 150°C before weighing. Potassium metaperiodate K_5IO_6 may also be used as a primary standard. It is stable if prepared in alkaline solution.

Reducing Agent

Redox titrations are often performed for metal analysis. Metals in their lower oxidation states are common reducing agents. This includes Fe^{2+}, Sn^{2+}, Mo^{3+}, W^{3+}, Ti^{3+}, Co^{2+}, U^{4+}, and VO^{2+}. Sodium thiosulfate, ($Na_2S_2O_3$) is one of the most widely used reductants in iodometric titrations. Other reducing agents include sodium arsenite and PAO. Iodometric titration is discussed separately in the next section.

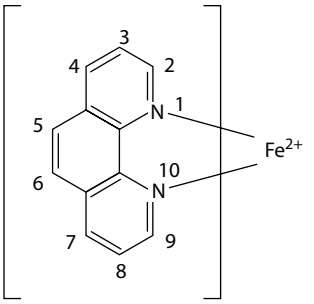
Oxalic acid is another common reducing agent. Many metals may be analyzed by reactions with oxalic acid. The metals are converted to their sparingly soluble metaloxalates that are then filtered, washed, and dissolved in acid. Acid treatment liberates oxalic acid, which is titrated with a standard permanganate or Ce^{4+} solution. Nitrous acid (HNO_2) is another suitable reducing agent. It may be analyzed by treatment with a measured excess of permanganate solution. Nitrous acid oxidizes to nitrate and the excess permanganate is back titrated.

Often a metal ion may be present in a solution in more than one oxidation state. To determine its total content, it should be converted into one specific oxidation state by treatment with an auxiliary oxidizing or reducing agent. Some of the preoxidants were mentioned earlier in this section. Among the auxiliary reducing agents, amalgamated zinc (Zn/Hg) and granular metallic silver are common. These are used in Jones and Waiden reductors, respectively. Other metals, such as Al, Cd, Ni, and Cu, are also used for the pre-reduction of analytes.

OXIDATION–REDUCTION INDICATORS

Redox indicators are substances that change color when they are oxidized or reduced. These substances have different colors in their oxidized and reduced states. The end point in the titration is detected from the change in the color. As in acid–base titration, color change occurs at a specific pH range. In redox titrations, the change in color depends on the change in the electrode potential of the system as the titration progresses. Protons (H+) reduce many indicators. Therefore, the transition potential and, hence, the color change is pH dependent too.

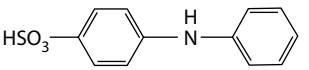
Ferroin is one of the most commonly used oxidation–reduction indicators. It is a 1,10-phenanthroline complex of iron having the following structure:

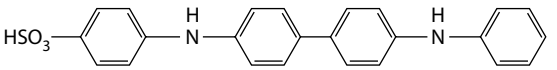


tris (1,10-Phenanthroline) iron (Ferroin)

Its oxidized form $(phen)_3Fe^{3+}$ is pale blue, while the reduced form $(phen)_3Fe^{2+}$ is red. The transition potential is about 1.11 V. Among the substituted derivatives of phenanthrolines, 5-methyl- and 5-nitro-1,10-phenanthroline complexes of iron have found wide applications in redox titrations.

Sulfonic acid derivatives of diphenylamine and diphenylbenzidine are suitable indicators in many redox titrations. The structures of these indicators are shown below:





The sodium salt of these acids may be used to prepare aqueous solutions of indicators. Other examples of redox indicators include starch, potassium thiocyanate (KSCN), methylene blue, and phenosafranine. Some selected general indicators in redox titrations are listed in Table 6.3. The properties of starch as an indicator in iodometric titration are discussed in the following section.

IODOMETRIC TITRATION

Iodometric titration involves the reaction of iodine with a known amount of reducing agent, usually sodium thiosulfate ($Na_2S_2O_3$) or PAO. Starch solution is used as an indicator to detect the end point of the titration. Thus, the exact amount of iodine that would react with a measured volume of sodium thiosulfate of known strength is determined. From this, the concentration of the analyte in the sample, which is proportional to the amount of iodine reacted with thiosulfate or PAO, is then calculated.

Iodometric titration is performed out in one of the following ways:

1. Potassium iodide solution in excess is added to the sample. An analyte such as chlorine liberates iodine from KI under acidic condition. The liberated iodine is directly titrated against standard $Na_2S_2O_3$ or PAO. The concentration of the iodine liberated is proportional to the concentration of the analyte in the sample. The reaction of chlorine with potassium iodide is as follows:

$$Cl_2 + 2KI \Rightarrow 2KCl + I_2 \uparrow$$

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Thus, the concentration of the analyte in the sample should be equal to

$$\text{mg analyte/L} = \frac{\text{mL titrant} \times \text{normality} \times \text{milliequivalent wt. of analyte}}{\text{mL sample}}$$

2. Other substances present in wastewater may consume the iodine produced before it reacts with the standard reducing agent. Thus, there is a good chance that some iodine may be lost; the whole amount of released iodine might not fully react with the standard reducing agent, $Na_2S_2O_3$ or PAO, which can produce erroneous results. This may be avoided by performing a back titration in which an accurately measured amount of the reducing agent is added to a measured volume of the sample. If the analyte were an oxidizing agent like chlorine, it would react with thiosulfate or PAO. The excess unreacted reducing agent is then measured by titrating with standard iodine or iodate titrant. At the end point, the solution turns from colorless to blue. The amount of reducing agent that reacts with the analyte is thus measured by subtracting the unreacted amount from the starting amount added to the sample. From this, the concentration of the analyte in the sample is calculated.
3. A measured volume of sample is added to a known quantity of standard iodine solution estimated to be in excess over the amount of analyte (e.g., sulfide) in the sample. The standard iodine solution should contain an excess of potassium iodide. The analyte reacts with iodine. This would cause a lowering of strength of iodine solution after the reaction. The normality of iodine is then determined from titration against a standard solution of sodium thiosulfate. The concentration of analyte in the sample, which is proportional to the amount of iodine consumed, is calculated as follows:

$$\text{mg analyte/L} = \frac{[(A \times B) - (C \times D)]}{\text{mL sample}} \times \text{mg equivalent wt. of analyte}$$

where:
A is the mL iodine solution
B is the normality of iodine solution
C is the mL $Na_2S_2O_3$ solution
D is the normality of $Na_2S_2O_3$ solution

The above equation is derived as follows:

$$\text{The amount of iodine consumed by the analyte} = \text{Starting amount of iodine} - \text{Leftover amount of iodine after reaction}$$

The starting amount of iodine is equivalent to $A \times B$. The leftover amount of iodine is equivalent to $A \times B_1$, where B_1 is the normality of iodine solution after reaction (the volume of iodine is constant).

$$\text{Volume of iodine} \times \text{its normality} = \text{Volume of thiosulfate} \times \text{its normality}$$

That is,

$$A \times B_1 = C \times D$$

or,

$$B_1 = \frac{C \times D}{A}$$

Thus, the amount of iodine consumed $= (A \times B) - (A \times B_1)$
or,

$$\left[(A \times B) - \left(A \times \frac{C \times D}{A}\right)\right]$$

or,

$$[(A \times B_1) - (C \times D)]$$

If 1 g equivalent weight of iodine reacts with 1 g equivalent weight (or 1000 mg equivalent weight) of the analyte present in a measured volume of sample, the concentration of analyte, as mg/L analyte

$$= \frac{[(A \times B_1) - (C \times D)] \times \text{milliequivalent wt. of analyte}}{\text{mL sample taken}}$$

EXAMPLE 6.5

In the titrimetric analysis of sulfide (S^{2-}), 100 mL of wastewater was added to 20 mL of 0.025 N iodine solution that contained potassium iodide and was acidified. The solution was titrated against 0.025 N $Na_2S_2O_3$ solution using starch indicator. The end point in the titration was obtained after the addition of 18.7 mL of titrant. Determine the concentration of sulfide in the sample.

$$\text{mg } S^{2-}/\text{L} = \frac{[(20 \times 0.025) - (18.7 \times 0.025)]}{100} \times 16{,}000$$
$$= 5.2$$

The equivalent weight of sulfide as per the reaction $S + 2I_2 \rightarrow S^{2-} + I^-$, is 32/2 or 16, because 1 mol S^{2-} (or 32 g S^{2-}) loses 2 mol electrons. Therefore, the milliequivalent weight is 16,000.

Role of Potassium Iodide

Potassium iodide, which is used in unmeasured but excess amounts in iodometric titration, is the source of iodine for many types of reactions. It dissociates to iodide anion, which then reacts with the analyte to produce iodine. Hypochlorite reaction is shown below as an example. By measuring the amount of iodine released, the concentration of the analyte in the sample can be determined.

$$2KI \rightarrow 2K^+ \, 2I^-$$
$$OCl^- + 2I^- + 2H^+ \rightarrow Cl^- + I_2 + H_2O$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Potassium iodide also enhances the solubility of iodine in water.

Reducing Agent

Sodium thiodulfate, $Na_2S_2O_3$ is the most commonly used reductant in iodometric titration. It is a moderately strong reducing agent. It reduces iodine to iodide ion. The thiosulfate ion is quantitatively oxidized to tetrathionate ion. The half-reaction is

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e$$

The equivalent weight of $Na_2S_2O_3$ in the above reaction is the same as its molar mass, that is, 158 (as 2 mol of thiosulfate generates 2 mol electrons). Thus, to prepare 1 N $Na_2S_2O_3$, 158 g salt is dissolved in reagent grade water and the solution is made up to 1 L. The solution of appropriate strength must be standardized before titration. One advantage of $Na_2S_2O_3$ over other reducing agents is that its solution is resistant to air oxidation. However, it may be noted that low pH, presence of Cu(II) ions, presence of microorganisms, solution concentration, and exposure to sunlight may cause thiosulfate to decompose to sulfur and hydrogen sulfite ion, as follows:

$$2S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + S_{(s)}$$

For this reason, the thiosulfate solutions need to be restandardized frequently.

PAO, C_6H_5AsO, is as effective as sodium thiosulfate in reducing iodine. It is more stable than thiosulfate. An advantage is that it is stable even in dilute solution. This substance is, however, highly toxic and is a suspected carcinogen. Because of its toxicity, its application is limited. One such application is in the amperometric titration of residual chlorine. The oxidation–reduction reaction of PAO is similar to thiosulfate. Its equivalent weight in iodine reaction is 168.

Standardization of $Na_2S_2O_3$

Potassium iodate (KIO_3), potassium hydrogen iodate ($KHIO_3$), potassium dichromate ($K_2Cr_2O_7$), and potassium ferricyanide ($K_3Fe(CN)_6$) are some of the primary standards commonly used to standardize sodium thiosulfate titrant.

An accurately weighted amount of primary standard is dissolved in water containing an excess of potassium iodide. Upon acidification, stoichiometric amounts of iodine are liberated instantly, which are titrated with thiosulfate titrant of unknown strength, decolorizing the blue starch–iodine complex at the end point. With potassium iodate, the ionic reaction is as follows:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

Therefore, 1 mol $IO_3^- \equiv 3$ mol I_2.

Since 1 mol of iodine reacts with 2 mol of thiosulfate as per the reaction:

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

therefore, 1 mol $IO_3^- \equiv 3$ mol $I_2 \equiv 6$ mol $S_2O_3^{2-}$.

As mentioned, other oxidizing primary standards are equally efficient. Thus, the molecular reaction of potassium dichromate with potassium iodide in the presence of a strong acid produces a stoichiometric amount of iodine as follows:

$$K_2Cr_2O_7 + 6KI + 14HCl \rightarrow 8KCl + 2CrCl_3 + 3I_2 + 7H_2O$$
$$1\,\text{mol}\,Cr_2 + O_7^{2-} \equiv 3\,\text{mol}\,I_2 \equiv 6\,\text{mol}\,S_2O_3^{2-}$$

EXAMPLE 6.6

0.1750 g KIO_3 was dissolved in water. A large excess of KI was added to the solution, which was acidified with HCl. The liberated iodine was titrated with $Na_2S_2O_3$ of unknown strength using starch indicator. 57.8 mL of thiosulfate solution was added to obtain the end point. Determine the molarity of $Na_2S_2O_3$.

$$1\,\text{mol}KIO_3 \equiv 3\,\text{mol}\,I_2 \equiv 6\,\text{mol}\,Na_2S_2O_3$$

$$0.1750\,\text{g}\,KIO_3 \times \frac{1\,\text{mol}\,KIO_3}{214.0\,\text{g}\,KIO_3} \times \frac{6\,\text{mol}\,Na_2S_2O_3}{1\,\text{mol}\,KIO_3}$$

$$= 0.004907\,\text{mol}\,Na_2S_2O_3 = 4.907\,\text{mmol}\,Na_2S_2O_3$$

(the formula weight of KIO_3 is 214.0)

$$\text{The molarity of } Na_2S_2O_3 = \frac{4.907\,\text{mmol}}{57.8\,\text{mL}} = 0.0849\,\text{M}$$

Starch Indicator

Starch solution is the preferred indicator in iodometric titration. Although iodine itself has a perceptible color at a concentration of 5×10^{-6} M (which is the equivalent of adding one drop of 0.05 M iodine solution in 100 mL), it cannot serve as its own indicator because the environmental samples are often dirty and not so clear.

Starch is composed of macromolecular components, α-amylose and β-amylose. The former reacts irreversibly with iodine to form a red adduct. β-Amylose, on the other hand, reacts with iodine forming a deep blue complex. Because this reaction is reversible, β-amylose is an excellent choice for the indicator. The undesired alpha fraction should be removed from the starch. The soluble starch that is commercially available principally consists of β-amylose. β-Amylose is a polymer of thousands of glucose molecules. It has a helical structure into which iodine is incorporated as I_5^-

When thiosulfate or PAO titrant is slowly added to the deep blue solution of starch–iodine complex, the reducing agent takes away iodine from the helix. At the end point, when all the iodine is lost, the solution becomes colorless.

A large excess of iodine can cause an irreversible breakdown of starch. Therefore, in indirect iodometric analysis, the addition of starch is delayed. It is added before the end point when there is not enough iodine left in the solution. This is indicated when the deep brown color of the solution (due to iodine) becomes pale yellow on the gradual addition of the reducing agent titrant. When the reducing agent is titrated directly with iodine, starch may be added at the beginning because the iodine liberated is not enough to decompose the starch.

ARGENTOMETRIC TITRATION

Argentometric titration involves the titrimetric determination of an analyte using silver nitrate solution as titrant. Its application in environmental analysis is limited to the determination of chloride and cyanide in aqueous samples. The principle of the method is described below.

Ag^+ preferentially reacts with the analyte to form a soluble salt or complex. During this addition, Ag^+ reacts with the analyte only, and not the indicator. But when all the analyte is completely consumed by Ag^+ and no more of it is left in the solution, the addition of an excess drop of silver nitrate titrant produces an instant change in color because of its reaction with the silver-sensitive

indicator. Some of the indicators used in the argentometric titrations are potassium chromate or dichlorofluorescein in chloride analysis and *p*-dimethylaminobenzalrhodanine in cyanide analysis. Silver nitrate reacts with potassium chromate to form red silver chromate at the end point. This is an example of a precipitation indicator, where the first excess of silver ion combines with the indicator chromate ion to form a bright red solid. This is also known as the Mohr method.

Another class of indicators, known as adsorption indicators, adsorb to (or desorb from) the precipitate or colloidal particles of the silver salt of the analyte at the equivalence point. The indicator anions are attracted into the counterion layer surrounding each colloidal particle of silver salt. Thus, there is a transfer of color from the solution to the solid or from the solid to the solution at the end point. The concentration of the indicator, which is an organic compound, is not large enough to cause its precipitation as a silver salt. Thus, the color change is an adsorption and not a precipitation process. Fluorescein is a typical example of an adsorption indicator in argentometric titration.

Often, greater accuracy may be obtained, as in Volhard type titration, by performing a back titration of the excess silver ions. In such a case, a measured amount of standard silver nitrate solution is added in excess to a measured amount of sample. The excess Ag^+ that remains after it reacts with the analyte is then measured by back titration with standard KSCN. If the silver salt of the analyte ion is more soluble than silver thiocyanate (AgSCN), the former should be filtered off from the solution. Otherwise, a low value error can occur due to overconsumption of thiocyanate ion. Thus, for the determination of ions (such as cyanide, carbonate, chromate, chloride, oxalate, phosphate, and sulfide, the silver salts of which are all more soluble than AgSCN), remove the silver salts before the back titration of excess Ag^+. On the other hand, such removal of silver salt is not necessary in the Volhard titration for ions such as bromide, iodide, cyanate, thiocyanate, and arsenate, because the silver salts of these ions are less soluble than AgSCN, and will not cause any error. In the determination of chloride by Volhard titration, the solution should be made strongly acidic to prevent interference from carbonate, oxalate, and arsenate, while for bromide and iodide analysis titration is carried out in neutral media.

EXAMPLE 6.7

A standard solution was prepared by dissolving 6.7035 g $AgNO_3$ in water to a volume of 1 L. What volume of KSCN of strength 0.0957 M would be needed to titrate 50 mL of this solution?

$$\underset{(1\,\text{mol})}{AgNO_3} + \underset{(1\,\text{mol})}{KSCN} \rightarrow \underset{(1\text{mol})}{AgSCN} + \underset{(1\,\text{mol})}{KNO_3}$$

The molar mass of $AgNO_3 = 169.87$. Thus, 6.7035 g $AgNO_3$

$$= 6.7035\ \text{g}\ AgNO_3 \times \frac{1\,\text{mol}\ AgNO_3}{169.87\,\text{g}\ AgNO_3}$$
$$= 0.03946\ \text{mol}\ AgNO_3$$

$$\text{The molarity of this solution} = \frac{0.03946\ \text{mol}}{1\text{L}} = 0.03946\ \text{M}$$

The amount of $AgNO_3$ contained in 50 mL of the standard solution = 0.05 L × 0.03946 mol = 0.001973 mol $AgNO_3$, which would require 0.001973 mol $AgNO_3$ × (1 mol KSCN/1 mol $AgNO_3$) = 0.001973 mol KSCN. Therefore, the volume of 0.0957 M KSCN solution that would contain 0.001973 mol KSCN = 0.001973 mol KSCN × 1L/0.0957 mol KSCN × 1000 mL/1L = 20.6 mL.

EXAMPLE 6.8

To analyze sulfide (S^{2-}) in an aqueous sample, 150 mL of the sample was made ammoniacal before argentometric titration. The sample required 10.45 mL of 0.0125 M $AgNO_3$ solution in the titration. Determine the concentration of the sulfide in the sample.

The reaction can be written as follows:

$$2Ag^+ + S^{2-} \rightarrow Ag_2S(s)$$

The number of moles of solute = molarity × volume (L). Therefore, the mole amount of $AgNO_3$ contained in 10.45 mL solution of 0.0125 M strength

$$0.0125 \times 0.01045\,\text{L}\ AgNO_3 = 0.0001306\ \text{mol}\ AgNO_3$$

This is also equal to 0.0001306 mol Ag^+.

The mass of S^{2-} that would react with 0.0001306 mol Ag^+

$$= 0.0001306\ \text{mol}\ Ag^+ \times \frac{1\,\text{mol}\ S^{2-}}{2\ \text{mol}\ Ag^+} \times \frac{32.07\ \text{g}\ S^{2-}}{1\,\text{mol}\ S^{2-}}$$
$$= 0.0020935\ \text{g}\ S^{2-} = 2.0935\ \text{mg}\ S^{2-}$$

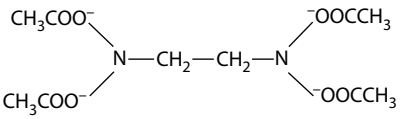
Thus, 2.0935 mg S^{2-} was present in 150 mL of the sample. Therefore, the concentration of sulfide in the sample

$$\frac{2.0935\ \text{mg}\ S^{2-}}{150\ \text{mL}} \times \frac{1000\ \text{mL}}{1\text{L}} = 13.96\ \text{mg}\ S^{2-}/\text{L}$$

COMPLEXOMETRIC TITRATIONS

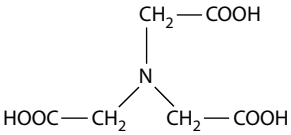
A complexometric titration is a rapid, accurate, and inexpensive method to analyze metal ions. However, its application in metal analysis in environmental samples is very much limited, because the more common atomic absorption/emission spectrometry method gives a lower detection limit.

Complexometric methods involve titrations based on complex formations. A ligand may have a single donor group, that is a lone pair of electrons, or two or more donor groups, to form coordinate bonding with metal ions. Such ligands are termed unidentate, bidentate, tridentate, and so on, depending on the number of binding sites in them. Thus, ammonia NH_3, having a lone pair of electrons, is an example of unidentate ligand, while glycin, an amino acid having two binding sites (one on the nitrogen atom and the other on the oxygen atom of the –OH group, after its H^+ is removed), is a bidentate ligand. A particular class of coordination compounds is known as a chelate. A chelate is produced when a ligand having two or more donor groups binds to the metal ion, forming a five- or six-membered heterocyclic ring. Ethylenediaminetetraacetic acid (EDTA) is probably the most widely used chelate in complexometric titrations. It is an aminopolycarboxylic acid having the following structure:



The molecule is a hexadentate ligand because it has six donor sites: the two nitrogen atoms and the four carboxyl groups. EDTA forms chelates with all metal ions combining in a 1:1 ratio,

irrespective of the charge on the metal ion. Such chelates have high stability too, because of their cage-like structures in which the ligand surrounds the metal ion, protecting the latter from solvation with solvent molecules. Another common chelate similar to EDTA is nitrilotriacetic acid (NTA), which has the following structure:



The cations may be analyzed either by direct titration or back titration. In the former method, a small amount of a metal that forms a less stable complex with EDTA than the analyte metal ion is added to the EDTA titrant. For example, magnesium or zinc forms a chelate with EDTA that is less stable than calcium chelate. Thus, in the determination of calcium in an aqueous sample, add a small quantity of magnesium into the standard EDTA titrant. Add a few drops of the indicator Eriochrome Black T into the sample. When the titrant is added onto the sample, calcium in the sample displaces the magnesium from the EDTA-magnesium chelate, forming a more stable chelate with EDTA. The liberated magnesium ions combine with the indicator producing a red color. The titration is continued. When the entire calcium ion is complexed with EDTA, any addition of excess EDTA titrant would result in the formation of magnesium-EDTA complex, causing a breakdown of the Mg-indicator complex. The latter breaks down because Mg-EDTA complex is more stable than the Mg-Eriochrome-black complex. Thus, at the end point of the titration, the red color of the solution decolorizes. Often, the titration is performed at pH 10.0, which is maintained by the addition of a buffer. At this pH, the color at the end point is blue. When the pH is greater than 10.0, metal hydroxides may precipitate out.

In the back-titration method, a measured amount of an excess standard EDTA solution is added to the sample. The analyte ion combines with EDTA. After the reaction is complete, the excess EDTA is back titrated against a standard solution of magnesium or zinc ion. Eriochrome Black T or Calmagite is commonly used as an indicator. After all the remaining EDTA chelates with Mg^{2+} or Zn^{2+}, any extra drop of the titrant solution imparts color to the indicator signifying the end point. The cations that form stable complexes or react slowly with EDTA can also be measured by the back titration method.

EXAMPLE 6.9

For the determination of Ca^{2+} in an aqueous sample, 50 mL of 0.01 M EDTA standard solution was added to a 100 mL sample. The excess EDTA was back titrated against 0.01 M EDTA standard solution to Eriochrome Black T end point. The volume of titrant required was 35.7 mL. Determine the concentration of Ca^{2+} in the sample.

$$50\text{ mL } 0.01\text{ M EDTA} \equiv \frac{0.01\text{ mol}}{1\text{ L}} \times 0.05\text{ L}$$
$$= 0.005\text{ mol or } 0.500\text{ mmol EDTA}$$

$$35.7\text{ mL } 0.01\text{ M } Zn^{2+} \equiv \frac{0.01\text{ mol}}{1\text{ L}} \times 0.0375\text{ L}$$
$$= 0.00375\text{ mol or } 0.375\text{ mmol } Zn^{2+}$$

Because EDTA combines with Zn^{2+} at 1:1 molar ratio, 0.375 mmol titrant (Zn^{2+}) would consume 0.375 mmol EDTA. Thus, the amount of EDTA that combined with Ca^{2+} in the sample

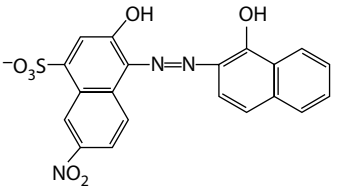
is 0.500 mmol − 0.375 mmol = 0.125 mmol, which also reacts in 1:1 molar ration with Ca^{2+}. Therefore, 100 mL of sample contains 0.125 mmol. Thus, the concentration of Ca^{2+} is

$$\frac{0.125\ \text{mmol}}{100\ \text{mL}} = 0.00125\ \text{M}$$

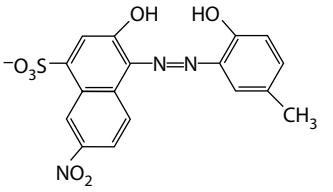
We can express the above concentration of Ca^{2+} in mg/L.

$$\frac{0.00125\ \text{mol}\ Ca^{2+}}{1\text{L}} \times \frac{40\ \text{g}\ Ca^{2+}}{1\ \text{mol}\ Ca^{2+}} \times \frac{1000\ \text{mg}\ Ca^{2+}}{1\ \text{g}\ Ca^{2+}} = 50\ \text{mg}\ Ca^{2+}/\text{L}$$

The mono- or disodium salt of EDTA may also be used in complexometric titrations. The formula weights of these salts in their dehydrated form are 372.3 and 349.3, respectively. EDTA, or its sodium salt, is standardized against a standard calcium solution. The indicators that are commonly used for such titrations are organic dyes. The structures of the two common indicators are as follows:



(Eriochrome Black T)



(Calmagite)

POTENTIOMETRIC TITRATION

Potentiometric titration can determine the end point more accurately than the color indicators. Thus, the quantitative consumption of a titrant in an acid–base neutralization, oxidation–reduction reaction, or complex formation reaction can be determined precisely and very accurately by potentiometric titration. The titration involves the addition of large increments of the titrant to a measured volume of the sample at the initial phase and, thereafter, adding smaller and smaller increments as the end point approaches. The cell potential is recorded after each addition. The potential is measured in units of millivolt or pH. As the end point approaches, the change in the electrode potential becomes larger and larger. The apparatus for potentiometric titration consists of an indicator electrode, a saturated calomel electrode, and a millivoltmeter or a pH meter with a millivolt scale. The selection of electrodes depends on the analytes and the nature of titration. For oxidation–reduction titrations, the indicator electrode should be made of an inert metal, such as platinum, palladium, or gold. Occasionally, silver and mercury are also used. Glass electrodes are commonly used in acid–base titrations. The mercury indicator electrode may be used in complexometric titrations involving EDTA. The stability of the EDTA complex with the analyte metal ion should be lower than the mercury-EDTA complex. Both the metallic, as well as the membrane, electrodes have been used in general complex formation titrations. In argentometric titrations involving the precipitation reactions of silver nitrate, a silver indicator electrode is used.

End Point Detection

The end point in a potentiometric titration can be determined by one of the following three methods: direct plot, first-derivative curve, and second-derivative curve.

The direct plot method is most commonly used to determine the end point. A titration curve is drawn by plotting the electrode potential in the *y*-axis against the mL titrant added in the *x*-axis. Near the end point, there is a sharp increase in potential. The midpoint of the steeply rising portion of the curve is taken as the end point of the titration (Figure 6.4).

A first-derivative curve may alternatively be constructed by plotting the change in the potential per unit volume, that is, ΔE/mL of titrant, added against the mL of the titrant. The curve would appear like a sharp peak, as shown in Figure 6.5. The end point is the volume corresponding to the highest ΔE/mL, that is, the tip of the peak.

The second-derivative curve method is similar to the first-derivative method. The only change is that the difference of ΔE, or the change in potential per mL (or $\Delta^2 E$/mL) of consecutive additions, are plotted against the volume of titrant added. Figure 6.6 shows the shape of the curve. It may be noted from the figure that very near after the end point, the data changes sign. The volume of the titrant in the *x*-axis that corresponds to the tip of the peak is the end point. Alternatively, the inflection point on the *x*-axis, at which $\Delta^2 E$/mL changes its sign, may be considered as the end point.

As an example, a set of data from a potentiometric titration is presented in Table 6.4. The method by which the calculations are performed is illustrated along with the data.

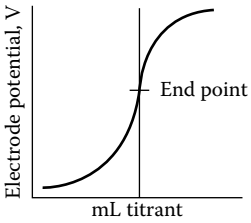


FIGURE 6.4 Direct plot.

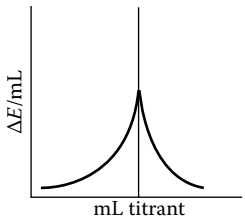


FIGURE 6.5 First-derivative curve.

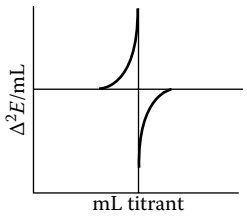


FIGURE 6.6 Second-derivative curve.

TABLE 6.4
Set of Potentiometric Titration Data as An Example

Titrant Volume (mL)	Electrode Potential (mV)	$\triangle E$/mL
5.0	58.2	3
10.0	72.3	4
15.0	91.4	8
17.0	107.0	14
18.0	121.5	14
18.5	132.5	22
18.8	144.8	34
19.00	156.0	60
19.10	170.0	140
19.20	202.0	320
19.30	284.2	820
19.40	251.1	330
19.50	235.4	160
19.60	228.3	70
19.80	220.3	40
20.10	212.4	24
20.60	208.0	16
21.60	200.0	8
23.60	190.2	5

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7 Colorimetric Analysis

Colorimetric tests can be carried out to analyze any substance in the aqueous phase for which a color-forming reaction is known. Its applications in both macro-, and microanalysis therefore are wide. In such methods, the analyte is identified from its reaction with a selective reagent to form a product that has a distinct color. The intensity of the color is measured by a spectrophotometer for quantifying the analyte concentrations. Many such reactions are known in the literature. Such tests usually are simple and of low costs for which no sophisticated instrumentations are necessary. The tests, however, may be prone to error from interference from the presence of compounds in the sample that have chemical properties similar to those of the analytes. Also, such tests may often be time consuming, in which getting a stable reading may take time. The test is carried out using light at a specific wavelength to measure the absorbance or transmittance of the solution. Such wavelengths are known in the literature for most common analytes. If not known, they can be determined by reading the absorbance or transmittance of a standard solution, setting the wavelengths at different values over a range. A detailed discussion is presented below.

Colorimetric methods are the most common and are widely employed in environmental wet analysis. Most anions, all metals, and many physical and aggregate properties can be determined by the colorimetric technique, which is fast and cost effective. However, the method may be unreliable for dirty and colored samples. Often, the presence of certain substances in samples can interfere with the test. In addition, if the color formation involves a weak color such as yellow, additional confirmatory tests should be performed. Despite these drawbacks, colorimetry is often the method of choice for a number of wet analyses.

Absorbance and *transmittance* are two important terms used in absorption measurement. If a beam of radiation of intensity P_0 passes through a layer of solution, a part of the light is absorbed by the particles of the solution; thus, the power of the beam weakens. The transmittance T of the solution is measured as the fraction of incident light transmitted by the solution. If the intensity of the transmitted light is P, then transmittance is measured as

$$T = \frac{P}{P_0}$$

Absorbance is measured in the logarithmic scale and is defined by the following equation:

$$A = -\log_{10} T = \log \frac{P_0}{P}$$

where A and T are the absorbance and transmittance of the solution, respectively. The absorbance of a solution is related to its concentration c by the following equation:

$$A = \log \frac{P_0}{P} = abc$$

where

b is the thickness of the solution (or the path length of radiation)

a is a proportionality constant called absorptivity

This is known as Beer's law. When the concentration is expressed in mol/L and b in cm, then a is termed as molar absorptivity, ε and Beer's law is modified to

$$A = \varepsilon bc$$

Thus, Beer's law exhibits a linear relationship between the absorbance of a solution to its path length and to its concentration. The relationship is very linear for path length, but not so for concentration. Beer's law works well for dilute solutions only. Solutions having concentrations greater than 0.01 M show significant deviation from Beer's law. Even in dilute solutions, the presence of an electrolyte, such as metal ions or chloride, sulfate or other anions, in large amounts, or the presence of large organic molecules can cause significant deviation from linearity. If the analytes dissociate or react with the solvent, or form adducts, then the molar absorptivity can change, causing departures from Beer's law. However, despite these limitations, Beer's law is extensively applied in environmental analysis, where the analyte concentrations encountered in the samples are generally well below 0.01 M. If the concentration is above the linearity range, the sample then must be diluted for measuring absorbance.

Beer's law applies only to monochromatic radiation, that is, light of one wavelength and not polychromatic radiation. The absorbance is measured by a spectrophotometer. Any polychromatic radiation source may be employed from which the desired single band wavelengths can be filtered by the grating or prism for the measurement of the absorbance. A tungsten lamp or tungsten/halogen lamp

TABLE 7.1
Common Pollutants

Analyte	Colored Complex/Derivative	Wavelength (nm)
Ammonia	Yellow mercuric salt, Hg_2OINH_2	415
	Indophenol	630
Bromide	Bromo derivative of phenol red	590
Chlorine residual	An oxidized form of *N*,*N*-diethyl-*p*-phenylenediamine	515
	An oxidized form of syringaldizine	530
Cyanide	Glutaconaldehyde derivative of barbituric acid	578
	Glutaconaldehyde derivative of pyrazolone	620
Fluoride	Zirconium dye	570
Iodide/iodine	Iodo derivative of methylidynetris(*N*,*N*-dimethylaniline)	592
Nitrate	Azo derivative of *N*-(naphthyl) ethylenediamine dihydrochloride	540
Ozone	Oxidized indigo	600
Phenols	4-Aminoantipyrine phenol complex	460
Phosphorus	Vanadomolybdophosphoric acid and its aminonaphthol sulfonic acid derivative	400–470
		815[a]
		650–815[b]
Silica	Molybdosilicic acid	410
Sulfate	Barium sulfate	420
Sulfide	Methylene blue derivative	664[a]
		600[b]
Sulfite	*Tris*(1,10-phenanthroline)iron(II)	510
Surfactants (anionic)	Methylene blue derivatives of sulfate esters and alkylbenzene sulfonates	652
Tannin and lignin	Phenol derivative of tungsto- and molybdophosphoric acid	700

[a] Absorbance only.
[b] Transmittance only.

is used as the light source. If transmittance is to be measured, then a filter photometer should be used. In environmental wet analysis, either a spectrophotometer or a filter photometer providing a light path of 1 cm or longer is used. It may be noted that absorbance and transmittance are inversely related. The greater the absorbance of a solution, the lower is its transmittance and vice versa.

Beer's law still applies even if a solution has more than one kind of absorbing substance. The total absorbance of the system would then be the sum of the absorbance of individual components, that is, $A_{\text{total}} = \varepsilon_1 bc_1 + \varepsilon_2 bc_2 + \ldots + \varepsilon_n bc_n$, where ε_1, ε_2, ε_n and c_1, c_2, c_n are the molar absorptivity and concentrations, respectively, of the absorbing components.

In colorimetric analysis, a reagent is selected that would form a colored complex or derivative with the analyte. Often, the analyte is extracted from the aqueous sample into an organic solvent before adding the color-forming reagent. Such extractions become necessary, especially for organic analytes such as phenols, lignin, and tannin.

Table 7.1 lists some common pollutants and their characteristic wavelengths (at which their absorbance or transmittance should be measured).

The first step in any colorimetric analysis is to prepare a standard calibration curve (i.e., a series of standard solutions of the analyte is made at a specific concentration range), which is then treated with the color-forming reagent, the absorbance or transmittance of which is then measured. The lowest calibration standard should be the minimum analyte concentration that would produce the least measurable absorbance or transmittance that should be the detection limit for the analyte. The highest calibration standard should be 10–15 times this concentration, and it must be within the linearity range. A plot is made between the absorbance or transmittance versus the concentration (or the microgram mass of the analyte). The concentration of the analyte in the sample is then read from the graph.

The presence of other substances in the sample that may react with the color-forming reagent can interfere with the test. These substances must be removed by precipitation or their interference effect must be suppressed by other means (such as pH control). These are discussed in detail throughout Section II of this book under colorimetric procedures for respective analytes.

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8 Analysis of Metals by Atomic Absorption and Emission Spectroscopy

Of the elements in the periodic table, more than two-thirds are metals. Although many of these metals are toxic, only some metals are major environmental pollutants because of their widespread use. The U.S. EPA has classified 13 metals as priority pollutants: aluminum, antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc. The Resource Conservation and Recovery Act has listed eight metals whose mobility in the soil is measured to determine the characteristic of toxic wastes. These metals include arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. All but one belong to the above list of priority pollutant metals.

Metals in general can be analyzed by the following techniques:

1. Colorimetry
2. Atomic absorption or atomic emission spectrophotometry

In addition, some metals may be determined by other methods, including ion-selective electrode, ion chromatography, electrophoresis, neutron activation analysis, redox titration, and gravimetry. Atomic absorption or emission spectrophotometry is the method of choice, because it is rapid, convenient, and gives the low detection levels required in the environmental analysis. Although colorimetry methods can give accurate results, they are time consuming and a detection limit below 10 μg/L is difficult to achieve for most metals.

Atomic Spectroscopy: An Overview

Technique	Principle	Comparison/Comments
Flame-AA	Atomic absorption: sample is vaporized and atomized in high-temperature flame. Atoms of the analyte element absorb light of a specific wavelength from a hollow cathode lamp, passing through the flame. The amount of energy absorbed by these atoms that is proportional to the number of atoms in the light path is measured. Components: lamp, flame, monochromator, and detector	Single element determination; detection limits relatively higher than other techniques
Furnace-AA	Atomic absorption: the flame is replaced by an electrically heated graphite tube, into which the sample is directly introduced. All of the analyte is atomized. This significantly enhances the sensitivity and detection limit. The general principle of this technique, otherwise, is same as the flame-AA	Single element determination; capability limited to fewer elements; analysis time longer than flame; the sensitivity and detection limits, however, are much greater than the flame technique, and significantly better than inductively coupled plasma (ICP) techniques

(*Continued*)

Atomic Spectroscopy: An Overview

Technique	Principle	Comparison/Comments
ICP	Atomic emission: atoms or ions of the element present in the sample absorb energy, causing excitation of their electrons to unstable energy states. When these atoms or ions return to their stable ground-state configuration, they emit light of specific wavelengths characteristic of the elements. ICP is an argon plasma that can heat the sample to a very high temperature in the range of 5500°C–8000°C. The sample is injected as an aerosol, and transported onto the ICP by argon, which is also used as a carrier gas. The emitted light is separated according to its wavelength and measured	Multielement determination (sequential or simultaneous); faster analysis time; minimal chemical interaction; detection limits and sensitivity fall in between that of the flame and graphite furnace measurements
ICP-mass spectrometry (ICP-MS)	The method combines an ICP with a quadrupole mass spectrometer. High-energy ICP generates singly charged ions from the atoms of the elements present in the sample. Such ions are now directed onto the mass spectrometer, separated, and measured according to their mass-to-charge ratio	Multielement determination; sensitivity and detection limits are exceptionally good (over 100 times greater than furnace techniques for some metals); isotopes may also be measured; also has the capability to determine nonmetals (at a much lower sensitivity); broad linear working range; high cost

SAMPLE DIGESTION FOR METALS

Aqueous and nonaqueous samples must be digested with an acid before their analysis by atomic absorption or atomic emission spectrophotometry. The metals and their salts present in the sample are converted into their nitrates due to the fact that the nitrates of all metals are soluble in water. Therefore, concentrated nitric acid by itself or in conjunction with hydrochloric acid, sulfuric acid, perchloric acid, or hydrofluoric acid is used in sample digestion for the determination of total metals. Nitric acid alone is, however, adequate for digestion of most metals. Table 8.1 lists the combinations of acids that may be helpful in sample digestion.

Acid digestion is performed using a small volume (5–10 mL) of nitric acid alone or in conjunction with one of the previously mentioned acids on a hot plate. Alternatively, a laboratory-grade microwave unit, specifically designed for hot acid digestion, can be used. When the sample is boiled with acid, the latter should not be allowed to dry. The acid extract after boiling and cooling is diluted with water to a measured final volume for analysis.

ATOMIC ABSORPTION SPECTROMETRY

An atomic absorption spectrophotometer consists primarily of a light source to emit the line spectrum of an element (i.e., the element to be analyzed), a heat source to vaporize the sample and

TABLE 8.1
Acid Combination Suggested for Sample Preparation

Acid Combination	Suggested Use
HNO_3–HCl	Sb, Sn, Ru, and readily oxidizable organic matter
HNO_3–H_2SO_4	Ti and readily oxidizable organic matter
HNO_3–$HClO_3$	Difficult to oxidize organic materials
HNO_3–HF	Siliceous materials

dissociate the metal salts into atoms, a monochromator or a filter to isolate the characteristic absorption wavelength, and a photoelectric detector associated with a microprocessor and a digital readout device for measuring the absorbance due to the metal at its corresponding concentration. The light source usually is a hollow cathode lamp or an electrodeless discharge lamp composed of the element to be measured. The heat source is an air–acetylene or air–nitrous oxide flame or a graphite furnace. In flame atomic absorption spectrometry, the heat source is a flame. The sample is aspirated into the flame and atomized. The light beam is directed through the flame. The metal atoms absorb energy at their own characteristic wavelength. The energy absorbed is proportional to the concentration of the element in the sample.

An atomic absorption spectrometer equipped with a graphite furnace or an electrically heated atomizer instead of the standard burner head gives better sensitivity and much lower detection limit than what is obtained with the flame technique (Table 8.2). The principle of this technique is the same

TABLE 8.2
Recommended Wavelength, Flame Type, and Technique for Flame Atomic Absorption Analysis

Element	Wavelength (nm)	Flame	Technique
Aluminum	309.3	N_2O–acetylene	DA, CE
Antimony	217.6	Air–acetylene	DA
Arsenic	193.7	Air–hydrogen	H
Barium	553.6	N_2O–acetylene	DA
Beryllium	234.9	N_2O–acetylene	DA, CE
Bismuth	223.1	Air–acetylene	DA
Cadmium	228.8	Air–acetylene	DA, CE
Cesium	852.1	Air–acetylene	DA
Chromium	357.9	Air–acetylene	DA, CE
Cobalt	240.7	Air–acetylene	DA, CE
Copper	324.7	Air–acetylene	DA, CE
Iridium	264.0	Air–acetylene	DA
Iron	248.3	Air–acetylene	DA, CE
Lithium	670.8	Air–acetylene	DA
Lead	283.3, 217.0	Air–acetylene	DA, CE
Magnesium	285.2	Air–acetylene	DA
Manganese	279.5	Air–acetylene	DA, CE
Molybdenum	313.3	N_2O–acetylene	DA
Nickel	232.0	Air–acetylene	DA, CE
Osmium	290.9	N_2O–acetylene	DA
Platinum	265.9	Air–acetylene	DA
Rhodium	343.5	Air–acetylene	DA
Ruthenium	349.9	Air–acetylene	DA
Silver	328.1	Air–acetylene	DA, CE
Selenium	196.0	Air–hydrogen	H
Silicon	251.6	N_2O–acetylene	DA
Strontium	460.7	Air–acetylene	DA
Tin	224.6	Air–acetylene	DA
Titanium	365.3	N_2O–acetylene	DA
Vanadium	318.4	N_2O–acetylene	DA
Zinc	213.9	Air–acetylene	DA, CE

Note: DA, direct aspiration; CE, chelation extraction; H, hydride generation.

as for the flame method. A small volume of sample is aspirated into a graphite tube that is heated in several stages. First, the sample is dried by low current heating. Then, it is charred at an intermediate temperature to destroy the organic matters and volatilize the compounds. Finally, it is heated to incandescence by a high current in an inert atmosphere to atomize the element. Atoms in their ground state absorb monochromatic radiation from the source. A photoelectric detector measures the intensity of the transmitted light. The intensity is inversely proportional to the number of ground state atoms in the optical path, that is, the greater the quantity of ground state atoms in the optical path, the greater the absorbance (in other words, the lesser the amount of light transmitted through).

The primary advantage of the graphite furnace technique over the conventional flame method is that the former requires a smaller volume of sample and the detection limit is much lower. Many metals can be determined at a concentration of 1 μg/L. A disadvantage of the graphite furnace technique, however, is that because of the high sensitivity, interference due to other substances present in the sample can cause a problem. Such interference may arise from molecular absorption or from chemical or matrix effects. This can be reduced or eliminated by correcting for background absorbance and by adding a matrix modifier into the sample. Some common matrix modifiers are listed in Table 8.3. Certain metals such as molybdenum, vanadium, nickel, barium, and silicon react with graphite at high temperatures, thus forming carbides. Such chemical interaction may be prevented by using pyrolytically coated tubes. Graphite tubes with L'rov platforms should be used. To prevent the formation of metallic oxides and minimize oxidation of furnace tubes, argon should be used as a purge gas.

Chelation–Extraction Method

Many metals at low concentrations can be determined by the chelation–extraction technique. These metals include cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, and zinc. A chelating agent such as ammonium pyrrolidine dithiocarbamate (APDC) reacts with the metal, forming the metal chelate that is then extracted with methyl isobutyl ketone (MIBK). A 100 mL aliquot of aqueous sample is acidified to pH 2–3 and mixed with 1 mL APDC solution

TABLE 8.3
Substances Added to the Sample for the Removal of Interference in Graphite Furnace Atomic Absorption Method

Element	Matrix Modifiers
Aluminum	$Mg(NO_3)_2$
Antimony	$Mg(NO_3)_2$ and $Ni(NO_3)_2$
Arsenic	$Mg(NO_3)_2$, $Ni(NO_3)_2$
Beryllium	$Mg(NO_3)_2$, $Al(NO_3)_3$
Cadmium	$Mg(NO_3)_2$, $NH_4H_2PO_4$, $(NH_4)_2SO_4$, $(NH_4)_2S_2O_8$
Chromium	$Mg(NO_3)_2$
Cobalt	$Mg(NO_3)_2$, $NH_4H_2PO_4$, ascorbic acid
Copper	NH_4NO_3, ascorbic acid
Iron	NH_4NO_3
Lead	$Mg(NO_3)_2$, NH_4NO_3, $NH_4H_2PO_4$, $LaCl_3$, HNO_3, H_3PO_4, ascorbic acid, oxalic acid
Manganese	$Mg(NO_3)_2$, NH_4NO_3, ascorbic acid
Nickel	$Mg(NO_3)_2$, $NH_4H_2PO_4$
Selenium	$Ni(NO_3)_2$, $AgNO_3$, $Fe(NO_3)_3$, $(NH_4)_6Mo_7O_{24}$
Silver	$(NH_4)_2HPO_4$, $NH_4H_2PO_4$
Tin	$Ni(NO_3)_2$, NH_4NO_3, $(NH_4)_2HPO_4$, $Mg(NO_3)_2$, ascorbic acid

(4% strength). The chelate is extracted with MIBK by shaking the solution vigorously with the solvent for 1 min. The extract is aspirated directly into the air–acetylene flame. Calibration standards of metal are similarly chelated and extracted in the same manner and the absorbances are plotted against concentrations.

APDC chelates of certain metals such as manganese are not very stable at room temperature. Therefore, the analysis should be commenced immediately after the extraction. If an emulsion formation occurs at the interface of water and MIBK, use anhydrous Na_2SO_4.

The chelation–extraction method determines chromium metal in its hexavalent state. In order to determine the total chromium, the metal must be oxidized with $KMnO_4$ under boiling and the excess $KMnO_4$ is destroyed by hydroxylamine hydrochloride prior to chelation and extraction.

Low concentrations of aluminum and beryllium can be determined by chelating with 8-hydroxyquinoline and extracting the chelates into MIBK and aspirating into a N_2O–acetylene flame.

Hydride Generation Method

Arsenic and selenium can be determined using the hydride generation method. These metals in the HCl medium can be converted to their hydrides by treatment with sodium borohydride. The hydrides formed are purged by nitrogen or argon into the atomizer for conversion into the gas-phase atoms.

The reaction with $NaBH_4$ is rapid when the metals are in their lower oxidation states as As(III) and Se(IV), respectively. Sample digestion with nitric acid, however, oxidizes these metals to their higher oxidation states, producing As(V) and Se(VI). These metals are reduced to As(III) and Se(IV) by boiling with 6 N HCl for 15 min. The digested sample is then further acidified with conc. HCl, treated with sodium iodide (for As determination only), and heated. A 0.5 mL $NaBH_4$ solution (5% in 0.1 N NaOH, prepared fresh daily) is added to this solution and stirred. The hydride generated (arsine or selenium hydride) is purged with the carrier gas such as argon and transported into the atomizer. Standard solutions of these metals are treated with $NaBH_4$ in the same manner for the preparation of the standard calibration curve. The presence of other substances in the samples causes little interference because hydrides are selectively formed and are removed from the solution. Commercially available continuous hydride generator units make the operation simpler than the manual method outlined above.

Cold Vapor Method for Mercury Determination

Cold vapor atomic absorption spectrophotometric method is applicable only for mercury analysis. The principle of this method is described below.

After acid digestion with nitric acid, mercury and its salts are converted into mercury nitrate. Treatment with stannous chloride reduces mercury into its elemental form, which volatilizes to vapors. Under aeration, the vapors of mercury are carried by air into the absorption cell. The absorbance is measured at the wavelength 253.7 nm. Prior to reduction, any interference from sulfide and chloride are removed by oxidizing the extract with potassium permanganate. Free chlorine produced from chloride is removed by treatment with hydroxylamine sulfate reagent and by sweeping the sample gently with air. After the sample is acid digested with conc. H_2SO_4 and HNO_3, the extract is treated with two strong oxidizing agents: $KMnO_4$ and potassium persulfate ($K_2S_2O_8$). After adding 15 mL of $KMnO_4$ solution (5%) to the acid extract, the solution is left to stand for 15 min. To this solution, about 10 mL of 5% $K_2S_2O_8$ solution is added. The mixture is heated to boiling for 2 h in a water bath. The excess of $KMnO_4$ is destroyed by adding NaCl-hydroxylamine sulfate solution [12% concentration of each, or a 10% hydroxylamine hydrochloride solution instead of $(NH_2OH)_2 \cdot H_2SO_4$].

Calibration standards are made from a water-soluble mercury salt, such as mercuric chloride. The standard solutions are analyzed first prior to the sample, following acid digestion, oxidation,

and reduction, as described above. A standard calibration curve is constructed by plotting absorbance versus concentrations of Hg (or mg Hg). The concentration of Hg in the sample is then determined by comparing the absorbance with that in the calibration curve.

ACCURACY IN QUANTITATION

Gross error and inaccuracy can often result at a very low level of detection, especially near the IDL. This is illustrated in the following data:

Concentration, μg/L	10	20	50	100
Absorbance	0.01	0.02	0.06	0.12

A calculation based on an absorbance reading of 0.01 at the IDL for an unknown sample can be inaccurate because there could be a large degree of fluctuation in absorbance readings at that level. For example, if five aliquots of a sample extract are aspirated into the flame, and if the absorbance is at the IDL, 0.01, there is a possibility of getting an erroneous reading. Let us suppose that the relative standard deviation of the measurement is 50%, which is not uncommon at the level of IDL. Then, the true absorbance reading may oscillate anywhere from 0.005 to 0.015. A concentration corresponding to a digital display of absorbance ranging from 0.00 to 0.02, as determined from the above calibration data, would correspondingly range between <10 and 20 μg/L. Thus, if 10 g of a sludge sample having a total solid content of 2% is acid digested and diluted to 1 L, then we may end up with a final result ranging between <50 and 200 mg/kg (dry weight corrected). Thus, we see how a minor deviation in the absorbance reading near the IDL can cause such a noticeable large deviation in the final result. Such errors occur frequently in routine analysis for metals in sludge samples. This can be prevented by increasing the sample concentration, that is, either by reducing the final volume of the extract, as in the above example, from 1 to 0.1 L or by increasing the amount of sample aliquot, say from 10 to 100 g for the digestion. A 10-time increase in the concentration of metal in the extract solution would produce an absorbance far above the IDL range, causing little deviation. In the above example, an absorbance reading in the range from 0.08 to 0.12 would correspond to a final, dry weight corrected result in the range of 33.5–60 mg/kg; and a reading between 0.09 and 0.12 would be equivalent to from 37.5 to 46 mg/kg.

Standard Addition

The method of standard addition should be performed to achieve accurate results. The method involves spiking an equal volume of standard solutions, at least three different concentrations to equal volumes of reagent grade water and sample aliquots, respectively. The absorbance is recorded and plotted in the *y*-axis against the concentration in the *x*-axis. The linear curve is extended through the *y*-axis. The distance from the point of intersection on the *x*-axis to the origin is equal to the concentration of the metal in the sample. An example is illustrated in Figure 8.1.

ATOMIC EMISSION PLASMA SPECTROSCOPY

Metals can be conveniently determined by emission spectroscopy using ICP. A great advantage of ICP emission spectroscopy as applied to environmental analysis is that several metals can be determined simultaneously by this method. Thus, multielement analysis of unknown samples can be performed rapidly by this technique. Another advantage is that, unlike atomic absorption spectroscopy, the chemical interference in this method is very low. Chemical interferences are generally attributed to the formation of molecular compounds (from the atoms) as well as to ionization and thermochemical effects. The principle of the ICP method is described below.

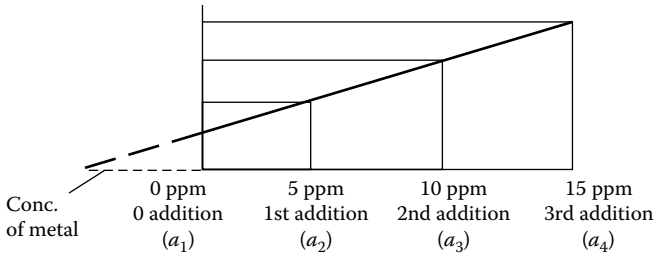

FIGURE 8.1 Linear curve showing standard addition method. Note: a1, 100 mL sample + 100 mL reagent grade water; a2, 100 mL sample + 100 mL 5 ppm standard; a3, 100 mL sample + 100 mL 10 ppm standard; and a4, 100 mL sample + 100 mL 15 ppm standard.

The apparatus consists primarily of an ICP source and a spectrometer. The spectrometer may be of simultaneous type (polychromator) or a sequential type (monochromator). The ICP source consists of a radio frequency generator that can produce at least 1.1 kW of power. It also has other components, which include torch, coil, nebulizer, spray chamber, and drain.

TABLE 8.4
Recommended Wavelength and the Instrument Detection Level in ICP Emission Spectrometry

Element	Wavelength Recommended (nm)	Alternate Wavelength (nm)	Approximate Detection Limit (μg/L)
Aluminum	308.22	237.32	50
Antimony	206.83	217.58	30
Arsenic	193.70	189.04	50
Barium	455.40	493.41	2
Beryllium	313.40	234.86	0.5
Boron	249.77	249.68	5
Cadmium	226.50	214.44	5
Calcium	317.93	315.89	10
Chromium	267.72	206.15	10
Cobalt	228.62	230.79	10
Copper	324.75	219.96	5
Iron	259.94	238.20	10
Lead	220.35	217.00	50
Lithium	670.78	–	5
Magnesium	279.08	279.55	30
Manganese	257.61	294.92	2
Molybdenum	202.03	203.84	10
Nickel	231.60	221.65	15
Potassium	766.49	769.90	100
Selenium	196.03	203.99	75
Silica (SiO_2)	212.41	251.61	20
Silver	328.07	338.29	10
Sodium	589.00	589.59	25
Strontium	407.77	421.55	0.5
Thallium	190.86	377.57	50
Vanadium	292.40	–	10
Zinc	213.86	206.20	2

A flowing stream of argon gas is ionized by an applied oscillating radio frequency field, which is inductively coupled to the ionized gas by a water-cooled coil. The coil surrounds a quartz torch that confines the plasma. A sample aerosol generated in the nebulizer and spray chamber is injected into the ICP, at a high temperature of 6000–8000 K of plasma. These high temperatures ionize atoms producing emission spectra. In addition, at this temperature, molecules of compounds formed completely dissociate, thus reducing any chemical interferences. The light emitted is focused onto a monochromator or a polychromator. The latter uses several exit slits to simultaneously monitor all configured wavelengths for multielement detection.

Spectral interferences from ion–atom recombination, spectral line overlaps, molecular band emission, or stray light can occur that may alter the net signal intensity. These can be avoided by selecting alternate analytical wavelengths and making background corrections.

The detection limit varies from element to element and is mostly in the low ppb range. Table 8.4 presents recommended wavelengths for metals analysis and their approximate detection limits.

ICP MASS SPECTROMETRY

Multielement determination of dissolved metals at ultra-trace level may be performed by ICP-MS. The U.S. EPA's Methods 200.8 and 1638 present a methodology for measuring trace elements in waters and wastes by the above technique. The sample is acid digested and the solution is introduced by pneumatic nebulization into a radio-frequency plasma. The elements in the compounds

TABLE 8.5
Recommended Analytical Masses for Element Detection

Element	Primary Isotope	Additional Isotope(s)
Aluminum	27	–
Antimony	121	123
Arsenic	75	–
Barium	137	135
Beryllium	9	–
Cadmium	111	106, 108, 114
Chromium	52	53
Cobalt	59	–
Copper	63	65
Krypton	83	–
Lead	206	207, 208
Manganese	55	–
Molybdenum	98	95, 97
Nickel	60	62
Palladium	105	–
Ruthenium	99	–
Selenium	82	77, 78, 80
Silver	107	109
Thallium	205	203
Tin	118	–
Thorium	232	–
Uranium	238	–
Vanadium	51	–
Zinc	66	67, 68

TABLE 8.6
Mass Ions for Internal Standards

Internal Standard	Mass
Lithium	6
Scandium	45
Yttrium	89
Rhodium	103
Indium	115
Terbium	159
Holmium	165
Lutetium	175
Bismuth	209

are atomized and ionized. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated by a quadrupole mass spectrometer by their mass to charge ratios. The mass spectrometer must have a resolution capability of 1 amu peak width at 5% peak height.

The ICP-MS technique is susceptible to interference that may arise from the presence of isobar elements (atoms of different elements having same masses) and isobaric polyatomic ions, buildup

TABLE 8.7
Interference from Isobars and Matrix Molecular Ions

Element	Mass	Isobar/Matrix Molecular Ion
Arsenic	75	$Ar^{35}Cl^+$
Chromium	52	$ClOH^+$, ArO^+, ArC^+
	53	$^{37}ClO^+$
	54	$^{37}ClOH^+$, ArN^+
Cadmium	106	ZrO
	108	MoO, ZrO
	111	MoO, ZrO
Copper	63	PO_2^+, $ArNa^+$, TiO
	65	TiO
Indium	115	^{115}Sn
Manganese	55	$ArNH^+$
Nickel	62	TiO
Scandium	45	$COOH^+$
Selenium	77	$Ar^{37}Cl^+$
	78	$^{40}Ar^{38}Ar^+$
	80	$^{40}Ar_2^+$
Silver	107	ZrO
	109	ZrO, MoO
Tin	115	^{115}In
Vanadium	51	$^{35}ClO^+$, $^{34}SOH^+$
Zinc	64	SO_2^+, S_2^+, TiO
	66	TiO

TABLE 8.8
Recommended Elemental Equations for Calculations

Element	Elemental Equation
Aluminum	(1.000) (^{27}C)
Antimony	(1.000) (^{121}C)
Arsenic	(1.000) (^{75}C)−(3.127) {(^{77}C)−(0.815) (^{82}C)}[a]
Barium	(1.000) (^{137}C)
Beryllium	(1.000) (^{9}C)
Cadmium	(1.000) (^{111}C)−(1.073) {(^{108}C)−(0.712) (^{106}C)}[b]
Chromium	(1.000) (^{52}C)[c]
Cobalt	(1.000) (^{59}C)
Copper	(1.000) (^{63}C)
Lead	(1.000) (^{206}C) + (1.000) (^{207}C) + (1.000)(^{208}C)[d]
Manganese	(1.000) (^{55}C)
Molybdenum	(1.000) (^{98}C)−(0.146) (^{99}C)[e]
Nickel	(1.000) (^{60}C)
Selenium	(1.000) (^{82}C)[f]
Silver	(1.000) (^{107}C)
Thallium	(1.000) (^{205}C)
Thorium	(1.000) (^{232}C)
Uranium	(1.000) (^{238}C)
Vanadium	(1.000) (^{51}C)−(3.127) {(^{53}C) − (0.113) (^{52}C)}[g]
Zinc	(1.000)(^{66}C)
Internal Standard	
Bismuth	(1.000) (^{209}C)
Indium	(1.000) (^{115}C) − (0.016) (^{118}C)[h]
Scandium	(1.000) (^{45}C)
Terbium	(1.000) (^{159}C)
Ytterbium	(1.000) (^{89}C)

Note: C, counts at specified mass (calibration blank subtracted).

[a] Correction for chloride interference with adjustment for ^{77}Se.

[b] Correction for MoO interference.

[c] There may be contribution from ClOH. This can be estimated from the reagent blank.

[d] For variable isotopes of lead.

[e] Isobaric elemental correction for ruthenium.

[f] Krypton might be present as an impurity in some argon supplies. Correction for ^{82}Kr is done by background subtraction.

[g] Correction for chloride interference with adjustment for ^{53}Cr.

[h] Isobaric elemental correction for tin.

of sample material in the plasma torch, transport and sample conversion processes in the plasma, quadrupole operating pressure, and ion energy. Such interferences may be minimized by using alternative analytical isotopes, correcting for elemental equation in data calculation, adjusting rinse times, diluting the sample extracts to reduce dissolved solids concentrations to less than 0.2% (w/v), and using appropriate internal standards similar to the elements being determined.

Recommended analytical masses, elemental equations, interference effects, and internal standards are summarized in Tables 8.5 through 8.8.

9 Ion-Selective Electrodes Analysis

Many ions, which include both metals and anions, may be analyzed rapidly and with a good degree of accuracy by ion-selective electrodes. In addition, dissolved gases, such as oxygen, carbon dioxide, ammonia, and oxides of nitrogen, can be analyzed by this technique using a gas sensor electrode.

A selective-ion electrode system constitutes the two half-cells that are a sensing electrode and a reference electrode, a readout meter, and a solution containing the specific ion to be analyzed. The sensing electrode could be a solid state, a liquid membrane, or a gas-sensing electrode, or the most familiar type, a glass electrode. The reference electrode should be either a single junction or a double junction type electrode containing a freely flowing filling solution and should produce a stable potential. A filling solution completes the electrical circuit between the sample and the internal cell. The filling solutions commonly used in the reference electrodes are KCl, AgCl, and KNO_3. A filling solution, however, must not contain the ion to be analyzed.

When a sensing electrode is immersed in a solution containing the same ion to which it is selective, a potential develops across the surface of its membrane. This potential is measured as voltage and is proportional to the concentration of the ion in the solution. The voltage caused by the sensing electrode is compared with a stable potential produced by a reference electrode.

The principle of electrode analysis is based on the Nernst equation that can be written as

$$E = E_o + S \log C$$

where

E is the measured voltage
E_o is the reference potential
S is the slope of the electrode
C is the concentration of the ion in the solution

In other words, the voltage difference between the sensing and the reference electrodes can be a measure of the concentration of the analyte ion that is selective to the sensor electrode. The above equation can be written as follows:

$$C_x + C_s \times 10^{\Delta E/S}$$

where

C_x and C_s are the concentrations of the unknown and the standardizing solutions, respectively
ΔE is the difference of potentials between that of the standardizing solution and the sample solution
S is the slope of the electrode that measures the change in electrode potential per tenfold change in concentration

ENVIRONMENTAL SAMPLE ANALYSIS

Selective-ion electrode technology has been successfully used to analyze many common pollutant anions, metal ions, and dissolved gas molecules in wastewater, drinking water, surface and

groundwater, sludges, soils, and solid wastes. The general analytical methods for solid matrix are the same as for water except that the solid sample, prior to analysis, is first extracted in water or into an aqueous phase with proper pH adjustment (Table 9.1).

Selective-ion electrodes are commercially available from Orion Research and many other manufacturers. Follow the manufacturer's instruction manual for the use and operation of the electrodes. The analysis may be performed by one of the following methods:

Standard calibration method
Standard addition method
Sample addition method

The electrode should be equipped with a readout device, such as a millivoltmeter or microprocessor.

Standard Calibration Method

In this method, a few milliliters of ionic strength adjuster (ISA) and/or a pH adjuster is added to both standards and samples before measurement. This sets the ionic strength of the samples and standards to a constant level.

Prepare at least two standards with one at concentrations below and one at concentrations above the expected range of sample concentrations. The concentration of higher standard should be 10

TABLE 9.1
Application of Ion-Selective Electrodes in Environmental Analysis

Analyte	Electrode Type	ISA
Ammonia	Gas sensing	pH adjusting ISA
Bromide	Solid state	5 M $NaNO_3$
Carbon dioxide	Gas sensing	CO_2 buffer[a]
Chloride	Solid state	5 M $NaNO_3$
	Liquid membrane	–
	Combination	–
Chlorine residual	Solid state	Iodide reagent
Cyanide	Solid state	5 M $NaNO_3$
Fluoride	Combination	TISAB[b]
	Solid state	–
Fluoroborate	Liquid membrane	2 M $(NH_4)_2SO_4$
Iodide	Solid state	5 M $NaNO_3$
Nitrate	Liquid membrane	2 M $(NH_4)_2SO_4$
Nitrogen oxide/nitrite	Gas sensing	Acid buffer
Oxygen, dissolved	Liquid membrane	–
Perchlorate	Liquid membrane	2 M $(NH_4)_2SO_4$
Sulfide	Solid state	SAOB[c]
Surfactant	Liquid membrane	–
Thiocyanate	Solid state	5 M $NaNO_3$

[a] Citrate buffer (sodium citrate/citric acid).
[b] Total ionic strength adjustment buffer (TISAB). It contains a buffer along with 1,2-cyclohexylenedinitrilotetraacetic acid and citrate or tartrate.
[c] Sulfide antioxidant buffer (SAOB) solution contains 0.2 M ethylenediaminetetraacetic acid disodium salt (disodium EDTA), 2 M NaOH solution, and ascorbic acid.

times greater than that of the lower standard. More standards may be prepared to plot calibration curves outside the linearity range.

Add ISA solution (or pH adjustor, as recommended in the instruction manual) to the most diluted standard. Set the instrument mode to read millivolts. Place the electrodes in the solution and record the stable millivolt reading. Repeat these steps and record the millivolt values for the higher concentration standard(s). Plot a calibration curve on a semilogarithmic paper, taking the millivolt values on the linear axis (y-axis) and the concentrations of the standards on the logarithmic axis (x-axis).

Rinse the electrodes and place them in the sample after adding ISA. Record the stable millivolt reading in the instrument mode. Determine the concentration of the sample from the calibration curve. Dilute the sample if the concentration of the analyte ion in the sample is high and it falls outside the calibration plot. Alternatively, prepare a new calibration plot adding more standards to bracket the concentration(s) of the sample(s).

Standard Addition Method

In this method, no calibration plot is required. The electrode potentials of the sample and then the sample plus a known amount of standard are recorded. The electrode slope is determined and the concentration of the analyte ion is calculated.

Determine the electrode slope following the instruction manual. Place electrodes in 100 mL or any suitable volume of the sample. Add a few milliliters of ISA and stir throughout. Set the instrument mode to read millivolts and record the stable millivolt reading, E_1.

Add a small, but accurately measured volume of standard to the sample that would produce a reading that is about twice the sample millivolt reading. The volume of the standard should not exceed 15% of the volume of the sample taken. The concentration of the standard is calculated as follows:

$$\text{Conc. of the standard to be spiked} = \frac{\text{Sample volume} \times \text{Estimated sample conc.}}{\text{Volume of standard to be spiked}}$$

For example, if the sample volume is 100 mL and the analyte concentration is estimated to be in the range of 2 ppm, add 5 mL of 40 ppm or 10 mL of 20 ppm of the standard.

Record the millivolt reading, E_2, after adding the standard. Record the value when the reading is stable.

The concentration, C_x, of the analyte ion in the sample may be calculated from the following equation:

$$C_x = \frac{\rho C_y}{[(1+\rho)\times 10^{\Delta E/S} - 1]}$$

where

C_y is the concentration of the standard
ρ is the ratio of the volume of spiked standard to the volume of sample taken
S is the electrode slope
ΔE is the millivolt difference, $E_2 - E_1$

EXAMPLE 9.1

Five mL of the 75-ppm chloride standard was added to 100 mL of a wastewater sample for chloride analysis. The initial millivolt reading for the sample was 17.5 mV. After adding the standard,

the reading was 35.3 mV. The slope was measured previously as 58.1 mV. Calculate the concentration of chloride in the sample.

$$C_y = 75\ \text{ppm}$$

$$\rho = \frac{5\ \text{mL}}{100\ \text{mL}} = 0.05$$

$$\Delta E = 35.3\ \text{mV} - 17.5\ \text{mV} = 17.8\ \text{mV}$$

$$S = 58.1\text{mV}$$

$$\begin{aligned} C_x &= \frac{0.05 \times 75\ \text{ppm}}{[(1+0.05) \times 10^{17.8\ \text{mV}/58.1\text{mV}} - 1]} \\ &= \frac{3.75\ \text{ppm}}{[(1.05 \times 10^{0.306}) - 1]} \\ &= \frac{3.75\ \text{ppm}}{[(1.05 \times 2.02) - 1]} \\ &= \frac{3.75\ \text{ppm}}{1.124} \\ &= 3.34\ \text{ppm} \end{aligned}$$

The concentration of chloride in the sample is 3.34 ppm.

Sample Addition Method

This method is very similar to the standard addition method described above. The only difference is that instead of adding the standard to the sample, the sample is added to the standard.

Determine the electrode slope before analysis as per the instruction manual. Place electrodes in 100 mL of the standard and add the ISA, stirring throughout. Set the instrument mode to read millivolts. Record the reading E_1 when it is stable.

Add a small but accurately measured volume of sample to the standard. The volume of the sample to be spiked should not exceed 15% of the volume of the standard taken. Select the concentration of the standard as follows:

$$\text{Conc. of the standard} = \frac{\text{Volume of sample to be spiked} \times \text{Estimated sample conc.}}{\text{Volume of standard taken}}$$

Read the millivolt value E_2 after adding the sample. Record the value when the reading is stable. Determine the concentration C_x of the analyte in the sample from the following equation:

$$C_x = [(1+\rho) \times 10^{\Delta E/S} - \rho] \times C_y$$

where

C_y is the concentration of the standard
ρ is the ratio of the volume of the standard taken to the volume of the sample spiked
ΔE is the millivolt difference $E_2 - E_1$
S is the electrode slope

10 Application of High-Performance Liquid Chromatography in Environmental Analysis

HPLC is a common analytical technique that is used to determine a wide range of organic compounds. Its application is widespread in industries such as dyes, paints, and pharmaceuticals. More than two-thirds of all organic compounds can be analyzed using HPLC methods. Its application in environmental analyses, however, has been relatively recent. Only a limited number of U.S. EPA methods are based on HPLC techniques.

The basic components of an HPLC system are (1) a pump with a constant flow control, (2) a high-pressure injection valve, (3) a chromatographic column, (4) a detector, and (5) a strip-chart recorder or a data system for measuring peak areas and retention times. Calibration standards are prepared at various concentrations and the retention times and peak areas of the analytes are compared against the standard solutions of analytes for their identifications and quantitations.

The analytes are separated by adsorption to a polar or nonpolar support surface or by partition into a stationary liquid phase. Silica is the most common polar adsorbent. HPLC involves the separation of compounds by partition on a stationary liquid phase, bonded to a support. The support, such as silica, is derivatized with a functional group that is covalently attached to the surface and is more stable than any coated phase. Such bonded phases can be used with most solvents and buffers. A mobile liquid phase transports the sample into the column where individual compounds are selectively retained on the stationary liquid phase and thus separated.

In normal phase liquid chromatography, a bonded polar surface, such as cyano-, diol-, or amino group bound to silica is employed, while the mobile phase is nonpolar. Such a technique is commonly used to separate steroids, aflatoxins, saccharides, and thalidomide. On the other hand, reversed phase liquid chromatography, a highly versatile technique, commonly applied in environmental analysis, uses a nonpolar surface and a polar mobile phase. Such nonpolar surfaces include octadecyl-, octyl-, methyl-, and diphenyl groups bound to silica or polymers and packed, usually as 5 μm particles. The pore sizes of these packings and the total surface area available determine the access of compounds in a certain range of molecular weights and their distribution or adsorption onto the surface. As a result, they are some of the factors that govern the selectivity. Many resin-based polymeric supports are used as alternatives to silica-based reversed phase columns for the analysis of basic compounds at high pH. While the silica-based bonded-phase packings are unstable above pH 7, new resin-based C-18 reversed phase columns are operational at a wide pH range of 2–13. Water–acetonitrile and water–methanol mixtures are commonly used as polar mobile phases in reversed phase liquid chromatography. A guard column is often used along with the primary column to protect the system and extend the life of the primary column. Various reverse phase columns under different trade names are now commercially available. Cation exchange resins have been employed for many analyses.

Postcolumn derivatization is usually performed to determine the compounds separated on the column. Such derivatization reactions can produce derivatives of the analytes that can be determined at a lower detection level at a greater sensitivity and free from interference.

Analytes are often derivatized to enhance the sensitivity of UV, fluorescence, conductivity, or electrochemical detectors. Such derivatizing reagents include ρ-bromophenacyl reagent for UV detection, and *o*-phthalaldehyde and dansyl chloride for fluorescence enhancement. In a postcolumn reaction, the effluent from the column is mixed with a reagent to form a derivative before it enters the detector. Absorbance detectors such as UV rays, or a photodiode array detector (PDAD), or a fluorescence detector is used in HPLC determination. A conductivity detector is used to detect inorganic substances. When using PDAD, interference can occur from many organic compounds at the shorter wavelengths (200–230 nm), at which they absorb light.

Fluorescence detectors are commonly used in many HPLC analyses. Compounds absorb light from a monochromatic light source and release it as fluorescence emission. The detector equipped with filters responds only to the fluorescent energy. Presence of trace impurities that fluoresce can cause interference in the test.

The performance of the HPLC system should be evaluated from the column efficiency and the symmetry of the peak. The column efficiency is determined as the number of theoretical plates, *N*, which should be greater than 5000. It is calculated as follows:

$$N = 5.54\left(\frac{RT}{W_{1/2}}\right)$$

where

N is the column efficiency (number of theoretical plates)

RT is the retention time of components (s)

$W_{1/2}$ is the width of component peak at half height (s)

The greater the value of *N*, the greater is the column efficiency. The peak asymmetry factor should be between 0.8 and 1.8, and is determined as shown in Figure 10.1.

The asymmetry factor, therefore, is

$$= \frac{\text{AB}}{\text{BC}} = \frac{13\,\text{mm}}{11\,\text{mm}} = 1.2$$

The asymmetry factor should be between 0.8 and 1.8.

The use of HPLC technique for analyzing various types of organic pollutants or its potential application is highlighted in Table 10.1.

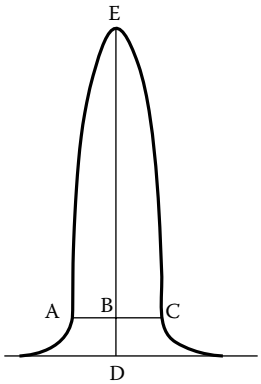

FIGURE 10.1 Asymmetry factor calculation. Peak height DE = 80 mm; 10% peak height = DB = 8 mm; peak width at 10% peak height = AC = 24 mm.

TABLE 10.1
Determination of Organic Analytes by HPLC

Analytes	Example(s)	Method
Aldehydes and ketones	Acrolein, methyl ethyl ketone	Sample extract buffered to pH 3 and derivatized with 2,4dinitrophenylhydrazine; derivative extracted and determined by UV at 360 nm
Polynuclear aromatic hydrocarbons	Anthracene, benzo(*a*) pyrene	Separated on a C-18 reverse phase column and detected by UV or fluorescence detector
Carbamate pesticides	Aldicarb, carbaryl	Separated on a C-18 reverse phase column, postcolumn hydrolysis with NaOH and derivatization with *o*-phthalaldehyde and 2-mercaptoethanol and fluorescence detection
Triazine pesticides	Atrazine, simazine	Separated on C-18 reverse phase column and detected by UV at 254 nm; mobile phase; acetonitrile: 0.01 M KH_2PO_4 (65:35)
Glyphosphate herbicides	*N*(phosphonomethyl) glycine	Postcolumn oxidation with CaOCl to glycine and derivatized with *o*-phthalaldehyde; fluorescence detection at 340 nm
Chlorophenoxy acid herbicides (also other chlorinated acids and chlorophenols)	2,4-D, silvex (dichlorobenzoic acid, picloram)	Sample acidified with H_3PO_4, analytes separated on an HPLC cartridge containing C-18 silica and measured by photodiode array UV detector
Nitroaromatics and nitramine explosives	TNT, tetryl, RDX	Separated on C-18 or CN reverse phase column and UV detection at 254 nm
Tetrazine explosive	Tetrazine	Separated on ion-pairing reverse phase column and UV detection at 280 nm
Phenols	Phenol, *o*-cresol, pentachlorophenol	Phenol and cresols converted to phenolates with NaOH; reverse phase HPLC, using an UV (at 274 nm), fluorescence, or electrochemical detector
Nitriles	Propionitrile, acrylonitrile	Separated on a C-18 reverse phase column and determined by UV detector
Amides	Acrylamide	Separated on a C-18 reverse phase column and UV detection
Phthalate esters	Diethyl phthalate, di-*n*-octyl phthalate	Separated on a C-18, or C-8, reverse phase high temperature bonded silica column and UV detection at 254 nm; also determined by gel permeation chromatography
Organic bases	Pyridine	Separated on a base-deactivated C-18 or C-8 reverse phase column and detected by UV at 254 nm
Azo dyes	Metanil yellow, Congo red	Separated on a C-18 reverse phase column and detected by an MS or UV detector
Chlorinated pesticides	Aldrin, endrin	Separated on a C-18, C-8, or CN- high-temperature bonded silica; mobile phase isooctane—ethyl acetate (97:3) and detected by UV at 254 nm
Benzidines	Benzidine	Separated on a C-18 reverse phase column and detected by an electrochemical detector
Barbiturates	Barbital, phenobarbital	Separated on a C-18 high carbon loaded silica column; mobile phase: methanol–water; detected by UV at 254 nm
Alkaloids	Cocaine, morphine	Separated on a C-18 high carbon loaded (20%) silica column; mobile phase: water (buffered with 0.02 M KH_2PO_4, pH 3)—acetonitrile (75:25); detected by UV at 254 nm

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11 Ion Chromatography

Ion chromatography is a single instrumental technique widely used for the sequential determination of many common anions in environmental matrices. Anions, such as NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, SO_3^{2-}, F^-, Cl^-, Br^-, I^-, oxyhalides, and many carboxylate ions, may be determined rapidly in a single sequential step. The main advantages of the ion chromatography technique are

1. Several anions can be determined in a single analysis.
2. It distinguishes halides (Br^-, Cl^-, etc.) and anions in different oxidation states (e.g., SO_4^{2-} and SO_3^{2-}, or NO_3^- and NO_2^-); such anions often interfere with each other in the wet analysis.
3. It is simple and rapid.

The method involves chromatographic separation of water-soluble analytes and the detection of separated ions by a conductivity detector. It can also be used to analyze oxyhalides, such as perchlorate (ClO_4^-) or hypochlorite (ClO^-), weak organic acids, metal ions, and alkyl amine. The analytes that can be determined by ion chromatography are listed in Table 11.1.

The aqueous sample is injected into a stream of carbonate/bicarbonate eluant. The eluant is pumped through an ion exchanger (a resin-packed column). Sample ions have different affinities for the resin; therefore, they move at different rates through the column, thus resulting in their separation. A strongly basic low capacity anion exchanger is used for the analysis of anions in the sample. The eluant and the separated anions then flow through a suppressor column, which is a strong acidic cation exchanger that suppresses the conductivity of the eluant to enhance the detection of the sample ions. The separated ions are now converted into their highly conductive acid form (i.e., NO_3^- converted to HNO_3) and measured by their conductivities. They are identified by the retention times and quantified by comparing their peak areas/peak heights against calibration standards. Conductivity detection offers a highly sensitive and specific detection mode for both inorganic and organic ions.

Sensitivity and detection levels of analyte ions can be dramatically improved by chemical suppression and auto-suppression techniques (Dionex Corp, 2009). In chemical suppression, the electrodes apply no electrical potential across, while in auto suppression, such a potential is applied to enable the transport of ions. This technique maximizes the sensitivity by increasing the analyte conductivity and reducing background conductivity and sample counter ions. This process is depicted in Figure 11.1 in two typical ion chromatograms. Furthermore, the capacity of the ion exchanger column increases, that is, the column can take a higher load of analyte ions without any peak distortion.

Eluants other than carbonate/bicarbonate have also found wide application in many environmental and nonenvironmental analyses. Some common eluants are listed in Table 11.2. Sodium hydroxide solution has now become an eluant of choice for many ion chromatography analyses using suppressed conductivity detection. The schematic representation of the method is outlined in Figure 11.2.

The Na ions from the eluant are removed at the suppressor column, and also the hydronium ions (from water electrolyzed) combine with the OH ions from the eluant to form water that is less conductive than the eluant NaOH. Thus, the net effects are (1) conductivity of the background NaOH eluant decreases and (2) the conductivity of the analyte anions increases, because they are now in their acid form. Both of these effects significantly enhance the signal-to-noise ratio, thus lowering the detection levels and increasing the sensitivity.

TABLE 11.1
Application of Ion Chromatography in Environmental Analysis

Analytes	Formula/Examples
Common inorganic anions	F^-, Cl^-, Br^-, I^-, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, SO_3^{2-}, CO_3^{2-}, PO_3^{3-}, HPO_4^{2-}, and CNO^-
Oxyhalides	ClO_4^-, ClO_3^-, ClO_2^-, ClO^-, BrO_4^-, BrO_3^-, IO_4^-, and IO_3^-
Pyrophosphate, polyphosphates, and metaphosphates	$P_2O_7^{4-}$, $P_3O_{10}^{5-}$, $P_4O_{13}^{6-}$, and $P_2O_6^{2-}$
Thiosulfate and thiocyanate	$S_2O_3^{2-}$ and SCN^-
Miscellaneous inorganic anions	CrO_4^{2-}, BO_3^{3-}, AsO_4^{3-}, SeO_4^{2-}, SeO_3^{2-}, MnO_4^{2-}, WO_4^{2-}, etc.
Metal ions (alkali and alkaline earth metals)	Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}
Common transition metal ions[a]	Fe^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, and Ni^{2+}
Ammonium ion	NH_4^+
Chromium hexavalent	Cr^{6+} [b]
Cyanide	CN^- [c]
Organic anions of carboxylic acid type	Acetate, formate, oxalate, maleate, phthalate, and tartrate
Sulfonated organic acids	Benzenesulfonate and ρ-toluenesulfonate
Chlorophenoxy acid herbicides	2,4-D, silvex, 2,4,5-T
Amines	Ethylamine, trimethyl amine, isobutylamine, morpholine, and cyclohexylamine

[a] Post column reaction with UV detection at 530 nm; eluant: pyridine-2,6-dicarboxylic acid.
[b] Post column colorimetric reaction and photometric detection, also by chemically suppressed ion chromatography with conductivity detection.
[c] Acid digestion followed by chemically suppressed ion chromatography.

Ion chromatography is the most convenient analytical approach for the determination of most inorganic anions, including oxyhalides in potable and wastewater and solid waste extracts. The U.S. EPA and the Standard Methods (U.S. EPA, 1993; APHA, AWWA, and WEF, 2005) have approved this method. Several columns are now commercially available (such as Ion Pac (Dionex Corp, 2009) or equivalent) that provide isocratic separation of common inorganic anions in less than 10 min using a carbonate/bicarbonate eluant and their detection at low ppm level employing a suppressed conductivity detector. In addition, by using gradient conditions and varying ionic strength by over two orders of magnitude, many mono-, di-, and trivalent ions can be separated in a single run. Such gradient ion chromatography with chemical suppression can prevent coelution and provide separation of a wide range of inorganic ions and organic ions. Many sulfonated

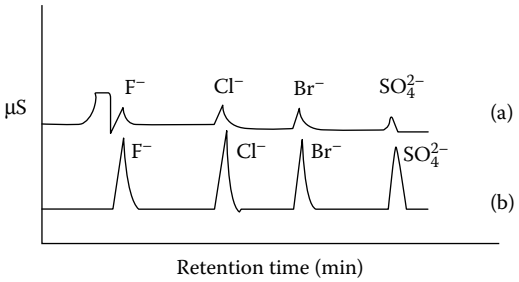

FIGURE 11.1 Ion chromatograms: (a) without suppression and (b) with suppression.

TABLE 11.2
Some Common Eluants Used in Ion Chromatography[a]

Eluants	General Applications
Sodium carbonate/sodium bicarbonate	Common inorganic anions: F^-, Cl^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}
Sodium hydroxide	Common inorganic anions: F^-, Cl^-, SO_4^{2-}; organic anions: acetate, citrate, and fumarate
Sodium tetraborate/boric acid	Common inorganic anions: F^-, NO_3^-, SO_4^{2-}; oxyhalides and carboxylates, such as acetate and formate
Methanesulfonic acid	Alkali and alkaline earth metal ions: Na^+, K^+, Ca^{2+}; ammonium
Methanesulfonic acid/acetonitrile gradient	Alkali and alkaline earth metal ions; Li^+, Na^+, K^+, Mg^{2+}, ammonium ion; alkyl amines: methyl amine, triethyl amine, and morpholine

[a] Detector: suppressed conductivity.

organic acids, which are often found in leachates from hazardous waste dump sites, can be determined by ion chromatography by varying both solvent and ionic strength in a gradient elution profile.

Ion chromatography has also been used in air pollution studies to measure anions and cations in an air impinger solution and air particulate extracts.

Ion exchange columns are composed of microporous polymeric resins (or stationary phases) containing styrene or ethyl vinylbenzene crosslinked with divinylbenzene. This is a porous and chemically stable core. A layer of ion exchange coating is bonded onto this resin core, producing a reactive surface.

For an anion exchange column, the coating particles are functionalized with alkyl quaternary amine or alkanol quaternary ammonium groups. The particle size of the coating substances, the pellicular type structures, and the degree of crosslinking in the microporous resin all determine the degree of resolution of anions on the column (Dionex Corp, 2009). Such columns are commercially available from many suppliers. A guard column is used to protect the separator column from organics and particulates.

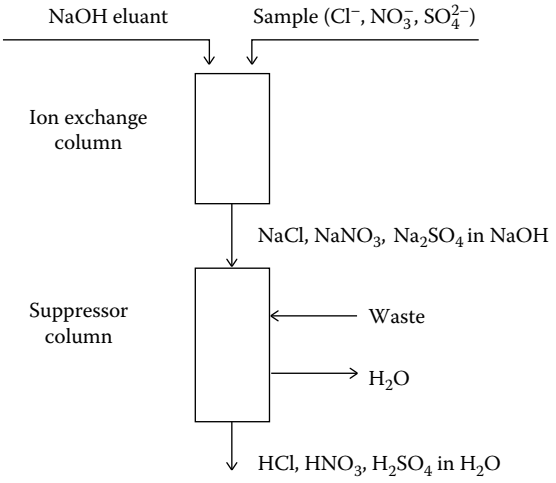

FIGURE 11.2 Schematic overview of sodium hydroxide elution method.

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12 Air Analysis

The techniques employed for air analysis are much different from those used to analyze either the aqueous or the solid samples. The most important part of air analysis is what is known as "air sampling," which involves techniques to trap or collect the organic or inorganic pollutants from the air. The volume of air sampled is very important to know to measure the final concentrations of the analytes in the air. Such measurements of volume of air, as well as the sampling techniques used, may be prone to error if not carried out properly. The instrumental analyses, however, are the same: GC, HPLC, or GC/MS may be used to identify and quantify the organic pollutants, atomic spectroscopy to determine the metals, and for the nuisance dusts and other particulate matters gravimetric methods may be adopted. Derivatization techniques may furthermore be applied, if such reactions are known, to convert the pollutants into their suitable derivatives for measurement. Portable instruments for in situ measurements of pollutants are not fully reliable.

Analysis of air, whether indoor or outdoor air, primarily consists of three steps: (1) sampling of the air, (2) chemical analysis of the sampled air, and (3) quality assurance to ensure the precision and accuracy of the measurement. Before performing the sampling, it is important to know the physicochemical properties of the target contaminants. In addition, sampling for outdoor air requires a proper sampling plan that includes the selection of proper sites for sampling based on weather conditions, topography, and other factors.

SAMPLING PLAN

The concentrations of contaminants in the atmosphere may vary significantly from time to time due to seasonal climatic variation, atmospheric turbulence, and velocity and direction of wind. The most important meteorological factors are (1) wind conditions and gustiness of the wind, (2) humidity and precipitation, (3) temperature, which varies with latitude and altitude, (4) barometric pressure (varying with the height above the ground), and (5) solar radiation and the hours of sunshine, which vary with the season.

The concentrations of the contaminants in the atmosphere and their dispersion in the air can be influenced by the topography, that is, whether the location of the polluting source is in a valley, plateau, or mountain, or near a lake or the sea. For example, mountains can act as barriers to airflow while valleys can cause persistence in wind direction.

In addition to the climatic conditions and topography, planning for sampling the ambient atmosphere should include a study on any noticeable effect caused by the pollutants on health and vegetation, and evaluation of any background information available. Based on these studies, which are part of sampling planning, the decision should be made on the sites' selection, the number of samples to be collected, and the time and frequency of sampling. Such planning can help to compare the ambient air quality at different locations, the geometric mean level of measured concentrations, and any trend or pattern that is observed.

For indoor air, a sampling plan should be prepared before performing the sampling. This is, however, somewhat different from the outdoor air sampling planning discussed above. The sampling scheme for the indoor air should be based on the following information:

1. Toxic symptoms observed in the occupants of the building and their case histories
2. Location of the building
3. Wind direction
4. Ventilation in the room

5. Humidity
6. Background information, if available, based on earlier studies (such as any previous air analysis report and the contaminants found)
7. The age of the house

The indoor air in very old houses may contain organics at trace levels due to what is known as the "sick building syndrome." The presence of low molecular weight organic compounds is attributed to the degradation of wood releasing hydrocarbons, aldehydes, and ketones.

Thus, for both the atmospheric air and the indoor air, it is essential to prepare a proper sampling plan prior to sampling of the air.

Air Sampling

Air sampling involves collecting a measured volume of air for chemical analysis. This is done in two ways: (1) collecting the air from the site in a container or (2) trapping the pollutants by passing a measured volume of air through a filter, an adsorbent, or absorbing solution. The principles of these methods are outlined below.

Direct Collection of Air

Air can be directly collected either in a Tedlar bag or a canister (e.g., SUMMA passivated canister) or a glass bulb. Canisters are best suited for air sampling. These are metal containers that can be chilled down to very low temperatures in a liquid nitrogen, helium, or argon bath. Air to be sampled can thus be condensed into the cryogenically cooled trap. Air may be collected either under high pressure using an additional pump or at a subatmospheric pressure by initially evacuating the canister. The canister can then be connected directly to the GC line. It may then be warmed or the sample air may be sucked in by a condensation mechanism into the GC column for analysis. Tedlar or other air collection bags or glass bulbs are equipped with inlet and outlet valves for the passage of air. The container to collect air is connected to a sampling pump (or a vacuum pump) and the air is then pulled in for collection. No cooling or condensation is required in such samplings.

Use of Adsorbent Tubes

Adsorbent tubes are commonly used for sampling air for organic analysis. Activated charcoal is one of the most widely used substances for trapping organics. Tenax and many other porous polymeric materials may be used for the same purpose. Silica gel is a common adsorbent for the adsorption of polar compounds such as alcohol. Adsorbent tubes for air sampling are commercially available, or may be prepared. Air is passed through the adsorbent in the direction as shown in Figure 12.1 by connecting the tube to the sampling pump. The tube has two sections—front and back—separated by a thin pad. Both sections are packed with the adsorbent, the larger quantity being filled in the

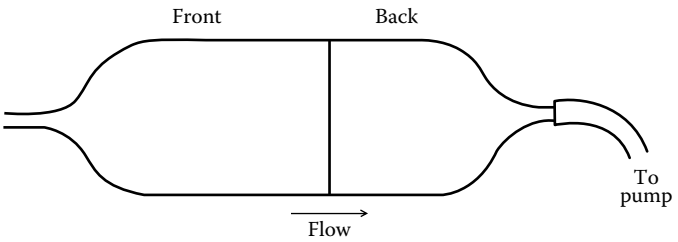

FIGURE 12.1 Adsorbent tube used for sampling of air for organic analysis.

front portion. If the amount of the analyte in the air is too high (more than what the front portion can hold to), or if the flow rate is too high, some of the analytes can pass through the front portion, but would be trapped over the adsorbent in the back. Thus, the total amount of analyte is the sum of the amounts that are trapped onto the front and the back sections, respectively.

For accurate analysis, we must know the total volume of air passed through the adsorbent tube, the mass of the analyte trapped, and the desorption efficiency (DE) of the solvent. Before sampling, the pump must be calibrated by using a bubble meter, a rotameter, or a gasometer to determine the flow rate. Using the flow rate and the time sampled, the total volume of air sampled can be determined.

The mass of the analyte can be measured from the chromatographic analysis. The analyte can be desorbed from the adsorbent surface either by a solvent (solvent desorption) or by heating (thermal desorption). In the former case, the selection of a solvent should be based on its DE, miscibility with the analyte, and chromatographic response. For example, carbon disulfide is a solvent of choice for many organics because of its high DE and poor chromatographic response to GC-FID. Similarly, isooctane and hexane are good solvents for chlorinated pesticides, because of their high DE and poor response to GC-ECD. On the other hand, a chlorinated solvent such as methylene chloride or chloroform should not be used if the analysis is to be performed by GC-ECD. This is because these solvents exhibit excellent response toward ECD, producing large peaks that can bury the small analyte peaks.

The DE of an appropriate solvent should be more than 85% and should be accounted for in the final calculation. If the DE for any specific compound is not known or not found in the literature, it can be determined by the following simple experiment.

Inject 5 μL of the analyte onto the adsorbent taken in a vial. Allow it to stand for 20–30 min. Add 10 mL of solvent and allow it to stand for an hour. Inject the eluant solution into the GC and record the area response, A_1. Now inject 5 μL of the analyte into another 10 mL portion of the solvent. Inject this solution onto the GC and record the area response, A_2. Dilute the sample and standard if peak overloading occurs. The DE is calculated as

$$\mathrm{DE} = \frac{A_1}{A_2} \times 100$$

Air Sampling for Particulates and Inorganic Substances

Dusts, silica, metal powder, carbon particles, and particulate matter are collected over membrane filters of appropriate pore size. Filter cassettes are used for this process. A membrane filter having the same diameter as the cassette is placed inside the cassette, one end of which is connected to the sampling pump. A measured volume of air is then sampled. While air can pass through the pores of the filter, the suspended particles are deposited on the filter.

Many water-soluble analytes can be sampled by bubbling the air through water in an impinger. Acid vapors, alkali vapors, or their dusts can be collected in water and their aqueous solutions analyzed by wet methods. Often, water is made basic or acidic to trap acidic or basic analytes, respectively. Other solvents can be used in the impinger, depending on the solubility of the analytes and the vapor pressure of the solvents. Certain organics in the air can also be trapped in impingers if one uses the proper solvents.

Flow Rate

An important step in air sampling is to determine the total volume of air to be sampled, to select the proper flow rate, and to measure the flow rate accurately. If the concentration of the analyte in the air is expected to be low, a large volume of air needs to be sampled. A high flow of air can reduce the contact time of analyte molecules over the adsorbent surface, thus reducing their adsorption.

Similarly, dissolution of the analyte in the impinger solvent is reduced under high flow rate. On the other hand, a low flow rate would require a longer sampling time. Thus, the flow rate and the total volume of air to be sampled depend on the nature of the analyte and its expected concentration. If the analysis is required for unknown contaminants of organic nature and if adsorbent tubes are used for sampling, a volume of 100–200 L air at a flow rate of 0.5–2 L/min should be suitable. If suspended particles are to be collected over membrane filters, a larger volume or air should be collected for accurate weight determination. In such cases, the airflow rate may be increased to reduce the sampling time.

As mentioned earlier, the personal sampling pump should be calibrated before and after sampling to determine accurately the flow rate and the volume of air sampled. A soap bubble meter or a gasometer should be used for such calibration.

CHEMICAL ANALYSIS

Most of the target organic compounds in air can be determined by GC using a FID. The analytes are desorbed into carbon disulfide, an aliquot of which is then injected into the GC-FID. GC using an ECD or any halogen-specific detector can determine halogenated organics. Likewise, the flame photometric detector can determine phosphorus and sulfur compounds. For GC analysis of nitrogen compounds, a nitrogen–phosphorus detector in nitrogen mode is the most effective. The photoionization detector can determine many aromatics and olefins. GC using a thermal conductivity detector can analyze low molecular weight gaseous hydrocarbons such as methane, ethane, and ethylene in air. A detailed discussion on GC analysis including the use of columns and detectors is presented in Chapter 3.

Unknown organic compounds can be identified and quantitatively measured by GC/MS. Analytes can be thermally desorbed from the adsorbent surface and analyzed by GC/MS. Alternatively, the bulk air from the site collected in a Tedlar or a canister can be injected or introduced by heating or suction into the system for separation and analysis.

High performance liquid chromatography, infrared spectroscopy, UV and visible spectrophotometry, and polarography are some of the other major analytical techniques used to determine many diverse classes of compounds.

Dusts, silica, and other suspended particles in the air are measured by gravimetry. The filter in the cassette should be weighted before and after sampling for accurate determination of the mass of the deposited particles. For metal analysis, the metal dusts deposited on the filter must be acid-digested and analyzed by atomic absorption spectrophotometry or inductively coupled plasma spectrometry. The inorganic anions in the impinger solution in their varying oxidation states can simultaneously be measured by ion chromatography. Colorimetry and ion-specific electrode methods can also be applied to determine individual ions. Among other analytical techniques, titrimetry methods involving acid–base titrations and redox titrations are often used to determine acidic, basic, and other inorganic analytes in the aqueous solutions in the impinger.

Analysis of specific groups of substances and individual compounds are discussed in Sections II and III of this book, respectively.

CALCULATION

The concentration of pollutants in air is generally expressed as mg/m^3 of air. This unit is used to express the concentrations for all kinds of analytes including organic compounds, metal ions, inorganic anions, and particulate matter. Another unit is ppm, which is often used to express concentrations of a specific compound. Conversion of ppm to mg/m^3 is as follows:

$$1\,\text{ppm} = \left(\frac{\text{Molecular weight of the compound}}{22.4}\right) \text{mg/m}^3 \text{ at STP}$$

where STP is the standard temperature and pressure which is 273°K and 1 atm (760 Torr), respectively. The molar volume at STP is 22.4 L.

The above relationship is derived as follows:

$$\text{Molecular density} = \frac{\text{One mole mass}}{\text{Molar volume of analyte in air at STP}}$$
$$= \frac{1\,\text{g MW}}{22.4\,\text{L}} \times \frac{1000\,\text{mg}}{1\,\text{g}} \times \frac{1000\,\text{L}}{\text{m}^3}$$
$$= \frac{\text{MW}}{22.4} \times 10^6 \times \frac{\text{mg}}{\text{m}^3}$$

or

$$\frac{1}{10^6} \times \frac{\text{Mass}}{\text{Volume}} = \frac{\text{MW}}{22.4}\,\text{mg/m}^3 \quad \left(\text{Substituting } \frac{\text{mass}}{\text{volume}} \text{ for density}\right)$$

where MW is the molecular weight.

That is,

$$1 \text{ part per } 10^6 \text{ part (mass/volume)} = \frac{\text{MW}}{22.4}\,\text{mg/m}^3$$

or,

$$1 \text{ ppm (weight/volume) at STP} = \frac{\text{MW}}{22.4}\,\text{mg/m}^3$$

or

$$1\,\text{mg/m}^3 = \frac{22.4}{\text{MW}}\,\text{ppm at STP}$$

For example, 1 ppm of cyclohexane at STP = (84/22.4) or 3.75 mg/m^3, or 2.93 mg/m^3 benzene at

$$\text{STP} = 2.93\,\text{mg/m}^3 \times \frac{22.4}{78} \times \frac{\text{ppm}}{1\,\text{mg/m}^3} = 0.85\,\text{ppm}.$$

Conversion of ppm to mg/m^3 or vice versa at any other temperature and pressure can be performed using one of the following two ways.

For example, air sampling of a compound is performed at an altitude where the temperature is 7°C and the pressure is 725 Torr. Conversion of ppm (W/V) to mg/m^3 can be calculated using either the combined gas equation or by the ideal gas equation as illustrated below.

From Boyles', Charles', and Gay-Lussacs' laws:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

where

P_1 is the initial pressure

V_1 is the initial volume

T_1 is the initial temperature

P_2 is the final pressure
V_2 is the final volume
T_2 is the final temperature

Temperature is always expressed in the Kelvin scale.
At STP $P_1 = 1$ atm, $V_1 = 22.4$ L (molar volume) and $T_1 = 0°C$ or 273 K.
In the given problem,

$$P_2 = 725\,\text{Torr} = 725\,\text{Torr} \times \frac{1\,\text{atm}}{760\,\text{Torr}} = 0.954\,\text{atm}$$

$$V_2 = ?$$

$$T_2 = 7°\text{C or } (7 + 273) = 280\,\text{K}$$

Therefore,

$$V_2 = \frac{1\,\text{atm} \times 22.4\,\text{L} \times 280\,\text{K}}{0.954\,\text{atm} \times 273\,\text{K}} = 24.08\,\text{L}$$

Thus, the molar volume at 7°C and 725 Torr = 24.08 L.
Therefore,
1 ppm analyte in air at 7°C and 725 Torr = MW of analyte/24.08 mg/m^3.
Thus, we need to determine the molar volume first at the given temperature and pressure conditions. This can also be determined from the ideal gas equation as follows:

$$PV = nRT$$

where
P is the pressure
V is the volume
T is the temperature
n is the number of moles of analyte
R is the ideal gas constant which is 0.082 L atm/mol K

In the above problem, $P = 0.954$ atm, $T = 280$ K and for 1 mol, $n = 1$.
Therefore,

$$V = \frac{nRT}{P}$$

$$= 1\,\text{mol} \times \frac{0.082\,\text{L atm}}{\text{mol K}} \times \frac{280\,\text{K}}{0.954\,\text{atm}}$$

$$= 24.07\,\text{L}$$

EXAMPLE 12.1

The concentration of sulfur trioxide in air at 15°C and 740 Torr was found to be 1.57 mg/m^3. Express this concentration in ppm (weight/volume).

At first, we have to determine the molar volume at 15°C and 740 Torr, either using combined gas laws or ideal gas equation. From the ideal gas equation

$$V = \frac{nRT}{P}$$
$$= 1\,\text{mol} \times \frac{0.082\,\text{L atm}}{\text{mol K}} \times \frac{288\,\text{K}}{0.974\,\text{atm}}$$
$$= 24.25\,\text{L}$$

where

$$P = 740\ \text{Torr} \times \frac{1\,\text{atm}}{760\ \text{Torr}} \text{ or } 0.974\ \text{atm}$$

$T = 273 + 15 = 288$ K
Therefore, ppm SO_3 at the pressure and temperature conditions of measurement

$$= \frac{\text{Concentration measured as mg/m}^3 \times \text{Molar volume}}{\text{MW}}$$
$$= \left(\frac{1.57 \times 24.25}{80}\right) \text{ppm} = 0.476\ \text{ppm}$$
$$\left[\text{i.e.,} \frac{1.57\ \text{mg}}{\text{m}^3} \times \frac{24.25\,\text{L}}{80\ \text{g}} \times \frac{1\,\text{g}}{1000\ \text{mg}} \times \frac{1\,\text{m}^3}{1000\,\text{L}} \times \frac{1{,}000{,}000\ \text{part}}{1\,\text{part}}\right]$$

EXAMPLE 12.2

A total volume of 300 L air was sampled for toluene using activated charcoal adsorbent. The analyte was desorbed with 2 mL carbon disulfide. An aliquot of the eluant was analyzed by GC. The concentration of toluene in the eluant was found to be 13.7 mg/L. Determine its concentration in the air as mg toluene/m^3 air.

Volume of air sampled = 300 L
Volume of CS_2 extract = 2 mL = 0.002 L
Toluene found in extract = 13.7 mg/L

$$\text{Mass of toluene in the extract} = \frac{13.7\,\text{mg toluene}}{1\text{L extract solution}} \times 0.002\,\text{L extract solution} = 0.0274\,\text{mg}$$

which came from 300 L air. Therefore, the concentration of toluene in the air

$$= \frac{0.0274\,\text{mg}}{300\text{L air}} \times \frac{1000\text{L air}}{\text{m}^3\ \text{air}}$$
$$= 0.091\,\text{mg/m}^3\,\text{air}$$

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13 Application of Immunoassay Techniques in Environmental Analysis

Enzyme immunoassay kits are now available for qualitative field-testing or for laboratory screening and semiquantitative analysis of pesticides, herbicides, PCBs, mononuclear and polynuclear aromatic hydrocarbons, pentachlorophenol, nitroorganics, and many other compounds in aqueous and soil samples. Certain analytes may be quantitatively determined as well, with a degree of accuracy comparable to gas chromatography or high-performance liquid chromatography determination. The method is rapid and inexpensive.

The analytical procedure consists of three steps: (1) sample extraction, (2) assay, and (3) color formation for the visual or spectrophotometric determination of the analyte in the sample. If a semiquantitative or quantitative analysis is desired, the concentration of the analyte can be determined from a calibration curve prepared by plotting absorbance or optical density against concentrations of a series of standards. The principle of immunoassay testing is described below.

Polyclonal antibodies of different types are known to show affinity for specific compounds. Thus, antibodies that can bind to a specific substance to be analyzed are immobilized to the walls of the test tubes, plates, or microwells. Such test tubes and plates are commercially available and supplied in the test kit. A measured amount (between 10 and 50 μL) of sample or sample extract is added to one such test tube containing an assay diluent (a phosphate buffer). An equal volume of analyte–enzyme conjugate (commercially available and supplied in the kit) is then added to the test tube. The enzyme conjugate is a solution containing the same analytes covalently bound to an enzyme. The solution mixture is incubated or allowed to stand for a specific amount of time. During this period, the enzyme conjugate competes with the analyte molecules for a limited number of antibody-binding sites in the test tube.

After the incubation, the unbound molecules are washed away, leaving behind the bound ones, anchored onto the antibody sites. Now a clear solution of a color-forming reagent (chromogenic substrate) such as, 3,3′,5,5′-tetramethylbenzidine is added to the mixture. The enzyme conjugate, bound to the antibody sites on the wall, reacts with the chromogenic substrate forming a blue color. The enzyme catalyzes the transformation of the substrate into a product that reacts with the chromogen, causing a blue color. The enzyme acts as a catalyst. Each enzyme molecule can rapidly catalyze the conversion of thousands of substrate molecules into product molecules that react with chromogen. In other words, the darker the color, the greater the amount of bound enzyme conjugate or, conversely, the lesser the amount of the analyte in the sample. Thus, the color intensity is directly proportional to enzyme conjugate concentration and, therefore, inversely proportional to the analyte concentration in the sample.

For qualitative screening, a visual comparison of color with standards can be made. However, for semiquantitative determination, a spectrophotometer should be used to read absorbance to plot a calibration standard curve. The color should be read as soon as possible because it becomes unstable after 30 min. The required period for incubation varies from substance to substance but can range from 5 to 10 min to 1 or 2 h. In certain analysis, the immunochemical reaction may require quenching after a specific amount of time. The reaction can be stopped by adding an acid, such as 1 N HCl that turns the blue to yellow. The intensity of yellow too can be measured to determine the analyte concentration in the sample.

An alternative assay procedure involves the use of antibody-coupled magnetic particles. Antibodies specific to the analyte of interest are covalently bound to paramagnetic particles rather than test tubes. The particles are suspended in buffered saline with preservative and stabilizers. Enzyme conjugate and the antibody-coupled magnetic particles suspension are then combined with the sample extract. The mixture is incubated. A magnetic field is applied to separate the magnetic particles that are then washed and treated with a color reagent. Blue develops on incubation. The reaction is then stopped by adding HCl, at which time the color turns yellow, and is read by a spectrophotometer.

Other assay procedures that can be employed involve the use of a coated particulate system or double antibody separation technique. These assay methods, including those discussed above, have both advantages and disadvantages when compared with each other. For example, in double antibody methods, an additional incubation period is required for the second antibody that increases the analysis time. Particulate systems require centrifugation to separate the bound particles. The more common coated-tube method is simple and rapid and does not involve centrifugation. However, its disadvantage is that the surface of the tube or plate limits the number of the antibody for the reaction. In addition, there may be loss of antibody because of absorption into the solid surface. An advantage of the magnetic particle method is that the antibody is covalently bound to the solid particles of uniform size (1 μm) giving even distribution throughout the reaction mixture. The method, however, requires the use of a magnetic field for separation.

Detection limits in the range of low ppb can be achieved by immunoassay testing for certain parameters in aqueous samples. For soil samples, detection limits of less than 10 ppm can be achieved for many contaminants.

The presence of substances having the same functional groups can interfere in the test, giving a false positive value. For example, 2,3,6-trichlorophenol may interfere in the test for pentachlorophenol. Such interference effect may, however, be reduced by using an antibody that is most selective for the target analyte.

EXTRACTION

Aqueous samples can be tested directly without any sample extraction steps. An aliquot of the sample (10–250 μL) should be suitable for the test. For high analyte concentrations, dilution of samples may be necessary. Follow the assaying procedure given in the kit using appropriate amounts of sample (or extract), enzyme conjugate, and coloring reagent.

Soil samples are extracted with methanol. A weighed amount of soil (e.g., 10 g) is shaken vigorously for 1 min with methanol and filtered. The filtrate is diluted (1:1000) with a diluent buffer solution. The extract is then immunoassayed for analysis.

CALCULATION

For soil, sediment, or solid waste samples, the concentration is calculated as follows:

$$\text{Concentration analyte, } \mu\text{g/g} = \text{Assay result } (\mu\text{g/L or ppb}) \times \frac{\text{Volume of extract (L)}}{\text{Mass of sample (g)}} \times \text{Dilution factor}$$

EXAMPLE 13.1

Soil weighing 10 g was extracted with methanol to a volume of 50 mL. A 100-μL aliquot of the extract was diluted to 25 mL. The assay result was 3.5 ppb. Determine the concentration of the analyte in the sample.

$$\text{Assay result} = 3.5\ \mu\text{g/L}$$
$$\text{Volume of extract} = 0.05\ \text{L}$$
$$\text{Sample weight} = 10\ \text{g}$$
$$\text{Dilution factor} = \frac{25\ \text{mL}}{100\ \mu\text{L}} = \frac{25{,}000\ \mu\text{L}}{100\ \mu\text{L}} = 250$$
$$\text{Conc. analyte, } \mu\text{g/g (ppm)} = \frac{3.5\ \mu\text{g}}{\text{L}} \times \frac{0.05\ \text{L}}{10\ \text{g}} \times 250 = 4.375\ \mu\text{g/g(ppm)}$$

Analyte concentrations in aqueous samples can be directly read from the standard curve. If the sample is diluted, the results must be multiplied by the dilution factor.

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14 Derivatization Reactions in Trace Chemical Analysis

DERIVATIZATION REACTIONS: GENERAL DISCUSSION

Pollutants containing various organic functional groups are often converted into their selective derivatives (products) for their detection. Derivatization reactions are widely used in many chromatographic and spectrophotometric analyses. In the colorimetric method, the substance to be analyzed must first be converted into a color-forming product by reacting with a suitable reagent, and the absorbance or the transmittance of such colored derivative is then measured at a specific wavelength using a spectrophotometer or a filter photometer. The literature on the colorimetric analysis abounds with such derivatization reactions. Likewise, in chromatography similar reactions are plentiful. The purpose of such derivatization is (a) to confirm the presence of a substance in the sample, more authentically as its derivative, using an appropriate gas chromatography (GC) or high-performance liquid chromatography (HPLC) detector, (b) to achieve better separation from the coeluting substances on the GC columns, (c) to obtain sharp chromatographic peaks, (d) to increase the volatility of compounds as their derivatives and therefore prevent any possible thermal decomposition at elevated temperatures, (e) to lower the levels of detection for substances analyzed, (f) to produce fluorescent derivatives or enhance fluorescence for HPLC analysis, and (g) to enhance sensitivity to UV detection. Sometimes a substance cannot be measured at all without converting it into one of its derivatives. For example, 2,4-dichlorophenoxyacetic acid (2,4-D), a herbicide used in agriculture and often found in many groundwater elutes as a broad and skewed peak in the sample chromatogram when analyzed in its acid form by GC, and therefore becomes difficult to measure. However, when this compound is converted into its methyl ester, the chromatographic peak is distinctly sharp, thus giving a far better resolution. Such derivatization reactions commonly are used in GC, GC/MS, HPLC, and liquid chromatography (LC)/mass spectrometry (MS) analyses. Also as mentioned above, often a lower detection limit with better resolution may be achieved only upon converting a compound into its appropriate derivative.

Another application of derivatization reactions is often to conveniently separate a substance from the sample matrix. For example, the lower molecular weight (MW) carboxylic acids and many disinfection by-products, haloacetic acids have moderate solubility in water. Their ester derivatives however are insoluble in water and can be extracted therefore by liquid–liquid extraction (LLE) using a water-immiscible extraction solvent, such as, hexane, toluene, or methylene chloride. As for the detection of a substance, conversion into a suitable derivative may sometimes becomes the only route for its GC, GC/MS, or HPLC measurement. In many HPLC analyses, postcolumn reaction is often carried out to convert the compounds after their separations on the column into their fluorescent derivatives, or sometimes enhance their fluorescence for their detection. Reagents such as *o*-phthalaldehyde and dansyl chloride are often used for such purposes. Postcolumn derivatization reactions are similarly carried out to enhance the UV detection in HPLC analysis, as for example, converting a substance to its *p*-bromophenacyl derivative enhances the sensitivity.

Compounds containing functional groups with active hydrogen atoms such as the –COOH, –OH, –NH, and –SH groups have the tendency to form intermolecular hydrogen bonds. This can affect their volatility and thermal stability. Also such functional groups may interact with the column packing materials. As mentioned earlier, carboxylic acids do not produce sharp peaks unless a polar

column is used. Also, the –COOH group may react with the column packing and shorten their lives. A very strong polar column therefore may be needed for analyzing such substances unless they are converted into suitable derivatives. Carboxylic acids are often esterified with alcohols using an acid catalyst such as dilute HCl, H_2SO_4, or BF_3. Methanol or diazomethane may also be used to convert such acids into their methyl esters. Such esterification may also be carried out by other routes using an acid chloride or an acid anhydride. Amides may alternatively be made instead of esters for such analysis. In aldehydes and ketones, the carbonyl functional group (C=O) may be derivatized effectively with 2,4-dinitrophenylhydrazine or semicarbazide to produce their corresponding phenylhydrazone or semicarbazone derivatives respectively for their GC detection by a nitrogen–phosphorus detector in N mode, or for their GC/MS analysis. The same reactions may also applied for their colorimetric detection. Practically any organic functional group in a compound may be derivatized using an appropriate reagent for its trace analysis by chromatography, MS, or colorimetry. Many examples of such derivatization reactions are presented below.

Many glyphosates are used as herbicides and found in environmental waters. Oxidation of glyphosates with calcium hypochlorite after their separation on column produces glycine, which is then reacted with *o*-phthalaldehyde to give a fluorescent derivative for HPLC analysis using a fluorescent detector. Similarly carbamate pesticides, such as aldicarb or carbaryl, widely used for crop protection, are derivatized for their HPLC detection. They are separated on a C-18 reversed-phase column, hydrolyzed by NaOH, and then reacted with *o*-phthaladehyde and 2-mercaptoethanol. Cholesterol, progesterone, testosterone, and other steroids and hormones require derivatization prior to their measurement. These substances are extracted first by LLE and then converted into their trimethylsilyl derivatives by reacting with N,O-bis(trimethylsilyl)-rifluoroacetamide and trimethylchlorosilane. The products are analyzed by high resolution MS. Among the derivatization reactions, alkylation, acylation, and silylation are the three general types of reactions that have wide applications in chromatography. These reactions are discussed below in detail.

ALKYLATION

Alkylation represents the replacement of an active hydrogen atom by an aliphatic or benzyl ($C_6H_5CH_2$–) group. Such reactions are used in GC to convert compounds, such as, carboxylic acids and phenols that contain acidic hydrogen into their ester derivatives. Esterification is one of the most common reactions. The general reaction with carboxylic acid using benzyl halide is shown below as an example:

$$RCOOH + C_6H_5CH_2X \rightarrow RCOOCH_2C_6H_5 + HX$$

(where R is an alkyl group and X is a halogen)

Also carboxylic acids can be converted into their esters by Fisher esterification reactions with alcohols using a mineral acid catalyst, such as HCl or H_2SO_4. An alternative catalyst is a Lewis acid, such as BF_3, dissolved in methanol to convert the lower carboxylic acids and fatty acids into their methyl esters for GC analysis. Methyl esters can also be prepared by reacting carboxylic acids with diazomethane, CH_2N_2, instead of methanol. Diazomethane is an unstable substance which can explode at high temperature and is also toxic. The reaction however is smooth and goes to completion. Diazomethane should be freshly generated and the apparatus to make this substance is commercially available. The esterification reaction of carboxylic acid with diazomethane is shown below:

$$RCOOH + CH_2N_2 \rightarrow RCOOCH_3 + N_2$$

Such alkylation reactions can also be used to prepare ethers, thioethers, thioesters, N-alkylamines, amides, and sulphonamide derivatives. In such alkylation, the products are less polar than the starting reactants because the active hydrogen is replaced by a nonpolar alkyl group. Some common derivatization reagents used in chromatography for carrying out alkylation reactions include boron trifluoride (BF_3) in methanol or butanol, tetrabutylammonium hydroxide (TBH), benzyl bromide, pentafluorobenzyl bromide, dialkylacetals, and diazoalkales.

If low MW carboxylic acids are to be converted into their butyl esters derivatives instead of methyl esters then TBH, formula $(CH_3)_4N^+OH^-$ should be used for such esterification. Butyl esters give longer retention times for GC analysis. The reaction is carried out at 60°C. The procedure is used for flash alkylation and can also be applied to low MW amines. The reactions with carboxylic acid and amine are shown below, respectively:

$$RCOOH + (CH_3)_4N^+OH^- \rightarrow RCOOC_4H_9 + NH_4OH$$

$$RNH_2 + (CH_3)_4N^+OH^- \rightarrow RNHC_4H_9 + NH_4OH$$

N,N-dimethylformamide dialkylacetals are effective derivatizing agents for acetylations and esterifications. They react with carboxylic acids, phenols, and thiols to give the corresponding alkyl derivatives. The reaction of N,N-dimethylformamide dimethylacetal or (DMF-dimethylacetal) (another name for this compound is 1,1-dimethoxytrimethylamine) with carboxylic acid is shown below as an example:

$$(CH_3)_2N - CH(OCH_3)_2 + R'COOH \rightarrow R'COOCH_3 + CH_3OH + (CH_3)_2NCHO$$

The reaction is fast, and occurs immediately upon mixing the substances. It is however moisture sensitive. Such reaction may be applied for flash alkylation and can be carried out in the injector port. DMF-dibenzylacetal, likewise, can be used to convert carboxylic acids into their benzyl esters. DMF-dimethylacetal can be used as a mild and selective reagent for many alkylation, formylation, and aminomethylation reactions. For example, 1,2-cyclohexanediol can be converted to cyclohexane epoxide, and heterocyclic thiols react with this reagent to produce S-methyl heterocycles in high yields. Notable among other dialkylacetals is 1,1-dimethoxy-N,N-dimethylmethylamine, $(CH_3)_2N$ — $C(CH_3)(OCH_3)_2$ which is an effective derivatization reagent for acetylation and esterification of carboxylic acids for GC or GC/MS analysis.

Pentafluorobenzyl bromide, formula $(C_6F_5)CH_2Br$ (PFBBr) is a suitable derivatizing agent for substances containing phenol, thiol, or carboxylic acid functional groups for their analyses by GC/MS in electron impact ionization mode or by ion trap MS. Also, the derivatives of these substances can be analyzed by GC-electron capture detector (ECD). The reactions are shown below for phenol, (C_6H_5OH) and a carboxylic acid with general formula, RCOOH. The reaction is carried out in presence of K_2CO_3 in 18-crown-6-ether solution. For phenol (or any phenolic substance), the product is an ether derivative, as shown below:

$$C_6H_5OH + (C_6F_5)CH_2Br \rightarrow C_6H_5OCH_2(C_6F_5) + HBr$$

The reaction with carboxylic acid, however, produces an ester derivative, as shown below:

$$RCOOH + (C_6F_5)CH_2Br \rightarrow RCOOCH_2(C_6F_5) + HBr$$

The carbonyl (>C = O) group in aldehydes and ketones can be converted into their pentafluorobenzyloxime derivatives at ambient temperature by reacting with O-(2,3,4,5,6-pentafluoro)benzyl

hydroxylamine hydrochloride (PFBHA) (the formula, $(C_6F_5)CH_2ONH_2$) in methanol. To carry out the reaction, add about 100 uL of reagent solution to a small volume of sample extract (about 1 mL) and let the solution stand for about 2 h. The final volume of the sample extract may be reduced under a gentle stream of nitrogen to an appropriate volume for the GC or GC/MS analysis. The reaction is shown below for ethyl methyl ketone as an example:

$$CH_3C(=O)C_2H_5 + (C_6F_5)CH_2ONH_2 \rightarrow (CH_3)(C_2H_5)C=N-O-CH_2(C_6F_5) + H_2O$$

ACYLATION

Acylation reactions involve substances that contain an aryl group and an active hydrogen atom forming their esters, thioesters, and amide derivatives. Such reactions are used in chromatography to convert compounds into their derivatives for better separation and greater response in detection than the parent compounds. For example, aldehydes containing active hydrogen may be derivatized with O-alkylhydroxylamines into their O-alkyloxime derivatives for their mass spectrometric determination. Similarly, in MS (electron impact ionization) converting a compound into its acyl derivative can modify its fragmentation pattern and provide useful information about the compound. In GC analysis insertion of perfluoroacyl groups into compounds enhances their detection by ECD. The presence of a carbonyl (>C=O) group adjacent to the carbon atom attached to fluorine or other halogens can enhance response to electron capture.

Among the acylation derivatization reagents, perfluoro acid anhydrides are most frequently used. They are used to convert alcohols, phenols, thiols, amines, and substances containing active hydrogen to their corresponding perfluoroacyl, derivatives especially for their mass spectrometric analysis. Also, these derivatives are stable and volatile for their applications in GC using flame ionization detector (FID), thermal conductivity detector (TCD), and ECD detectors. Such fluorinated anhydrides include trifluoroacetic acid anhydride, $F_3C–C(=O)–O–C(=O)–CF_3$, pentafluoropropionic acid anhydride, $CF_3–CF_2–C(=O)–O–C(=O)–CF_2–CF_3$, and heptafluorobutyric acid anhydride, $CF_3–CF_2–CF_2–C(=O)–O–CF_2–CF_2–CF_3$. The fluorinated anhydride and other derivatives may be prepared *in situ* in very small amounts for their direct injections. They are however moisture sensitive and care must be taken in their handling. Their preparation methods are described in the product literature. A few preparative methods are highlighted below. It may be noted here that the fluorinated anhydrides also produce their corresponding perfluoro acids as by-products in the reactions which must be removed from the reaction mixture before injecting the derivatives. Such by-products acids may be neutralized with amine bases, such as triethylamine for better results. The reactions however may be carried out directly without using an amine base but using a base that increases the product yield.

For example to carry out the derivatization reaction, a sample of trace amounts (about 0.1 ug) dissolved in 0.5 mL of solvent is combined with 0.2 mL of 0.05 M triethylamine in a small vial. The solvent used for this purpose should be a water-immiscible, volatile, and a nonhalogenated solvent having density less than that of water, such as benzene or toluene. Then, add 25 uL of fluorinated anhydride derivatizing reagent into this mixture. Cap the vial and heat it at about 50°C for 10–15 min. The mixture is then cooled down to below 20°C. To this product mixture, add 2 mL of distilled water, and shake for 1 min and then add about 1 mL of 5% aqueous ammonia solution. The mixture is centrifuged for a few minutes to separate out the clear immiscible organic layer at the top containing the product derivative from the bottom aqueous layer. An amount of 1 uL of the top layer of the product solution is injected onto the GC for analysis by ECD. The solution may be diluted or the quantities of the reactants may be adjusted accordingly within the scale.

Amines, amides, alcohols, and phenols may be derivatized into their fluoroacyl derivatives using fluorinated acylimidazoles. The general procedure is similar to the above steps. About 0.1–2 mg of sample is combined with 200 uL fluoroacylimidazole in a small vial. The mixture is heated at 60°C

TABLE 14.1
Some Acylation Reagents and Their Physical Properties

Name	MW	Density[a]	BP[b]
Trifluoroacetic acid anhydride	210.0	1.490	40.0
Pentafluoropropionic acid anhydride	310.0	1.571	69.5
Heptafluorobutyric acid anhydride	410.0	1.665	106.5
N-Methylbis(trifluoroacetamide)	223.1	1.550	123.0
Trifluoroacetylimidazole	164.1	1.560	39 (15 Torr)
Heptafluorobutyrylimidazole	264.1	1.562	57 (10 Torr)

[a] In g/cm^3 at 20°C.
[b] In °C.

for 15–30 min and the product solution is directly injected onto the GC for analysis of derivatives by an FID. Commonly used fluorinated acylimidazoles in derivatization reactions include trifluoroacetyl imidazole and heptafluorobutyl imidazole.

Many alcohols, thiols, and primary and secondary amines can be derivatized using N-methylbis(trifluoroacetamide) under mild nonacidic conditions. About 100–200 uL of this fluoroactamide reagent is added to 1–10 mg of sample dissolved in 1 mL of dimethylformamide, tetrahydrofuran, or acetonitrile and heated in a capped vial at 60°C–90°C for 15–30 min. Alternatively, the sample may be added to the fluoroacetamide solution made from the above solvents. The product solution after cooling down to room temperature may then be injected for GC analysis.

Several other acylation reagents are known and their applications have been documented in the chromatography literature. The product derivatives in these reactions may also be identified by MS. Few such derivatizing reagents are summarized in Table 14.1 along with their MWs, densities, and boiling points. The structural features and the reactions of a few selected perfluoro anhydrides with alcohols, thiols, and amines have been highlighted above.

Derivatization of amines, effectively are carried out by acylation reactions, though other methods involving nonacylation routes are well known. Such acylating reagents for amines include acyl chlorides, acid anhydrides, acyl amides, and acyl imidazoles. These reagents react with amino groups under mild conditions. The general reactions involving primary and secondary amines with acid anhydrides, acid chlorides, and acid amides are shown below, respectively. The reactions with imidazoles are discussed above for amines, alcohols, phenols, and amides.

Anhydride: $RR'NH + R''C(=O)–O–C(=O)R'' \rightarrow RR'NC(=O)R'' + R''COOH$
Acid chloride: $RR'NH + R''C(=O)Cl \rightarrow RR'NC(=O)R'' + HCl$
Acid amide: $RR'NH + [R''(C=O)]_2NCH_3 \rightarrow RR'NC(=O)R'' + R''C(=O)NHCH_3$

SYLILATION

Sylilation reactions involve replacement of active hydrogen from acids, alcohols, thiols, amines, and amides with trimethylsilyl groups. Enolizable aldehydes and ketones likewise are converted to their trimethylsilyl derivatives. Nonvolatile samples are converted into volatile silyl derivatives for their GC analysis. Also, the substitution of active hydrogen atom with silyl group in the molecule reduces the hydrogen bonding and polarity in the compound. Many hydroxyl and amino compounds are nonvolatile and often unstable above 250°C. Silylation yields more stable and volatile derivatives and therefore is an effective pathway to analyze such substances. Silylation involves nucleophilic

substitution reaction of the second-order proceeding through the SN_2 mechanism. For example, the substitution of active hydrogen in a compound containing –OH functional group using trimethylchlorosilane as a silylation reagent would yield the corresponding trimethylsilyl derivative as the end product. The reaction is shown below:

$$\text{Sample} - \text{OH} + (\text{CH}_3)_3\text{SiCl} \rightarrow \text{Sample} - \text{O} - \text{Si}(\text{CH}_3)_3 + \text{HCl}$$

The ease of reactivity of functional groups toward silylation follows in the order: alcohol ($1^\circ > 2^\circ > 3^\circ$) > phenol > carboxylic acid > amine > amide.

Silyl reagents are generally moisture sensitive and therefore stored in sealed containers. Pyridine or another base may be used as a solvent to drive the reaction in the forward direction. The solvent used should be pure and in small amount. The need of a solvent may be eliminated by directly mixing the compound with the silyl reagent and heating gently below 60°C for 10–15 min. Many sylilation reagents are known for such derivatization. They include trimethylchlorosilane, trimethylsilyldimethylamine, bis(trimethylsilyl)acetamide, trimethylsilylimidazole, bis(trimethylsilyl) trifluoroacetamide, hexamethyldisilzane, and many halomethylsilyl derivatization reagents. The reactivity and the selectivity however may differ with the reagent used.

DIAZOTIZATION

Substances may be diazotized to produce their diazonium salts which are then combined with coupling reagents to form colored azo dyes for their determination by spectrophotometry. The products usually have intense and characteristic colors. In such diazotization reactions, the nitrite anion (NO_2^-) is converted into an azo intermediate (tetravalent N with a positive charge on it). An example is the reaction of nitrite ion with sulfanilamide to produce a diazonium salt which is then reacted with N-(1-naphthyl)ethylenediamine to form an intense colored azo derivative. This is an example of a typical colorimetric test involving diazotization and coupling reactions. The reaction steps are presented in Chapter 39. The same test may be applied to measure nitrate, however after reducing the nitrate ion into nitrite, which is then subjected to diazotization and coupling. The reduction of nitrate to nitrite may be carried out effectively using cadmium or $SnCl_2$ or any other suitable reducing agent.

SELECTION OF DERIVATIZING REAGENT

Selecting a suitable reagent to convert a substance into an appropriate derivative for its analysis depends on the functional group present in it. It also depends to a great extent on what analytical technique is used. For example, when the detector sensitivity to ultraviolet absorption for an alcohol is zero or low at the wavelength 254 nm, a chromophore can be attached by reacting the alcohol with 3,5-dinitrobenzoyl chloride to enhance its UV absorption for HPLC-UV analysis. Similarly, the formation of fluorescent derivatives allows the detection of nonfluorescent molecules. Many reagents are known for such fluorescent derivatization. The trifluoro group, for example, is used commonly for sensitizing molecules for detection by electron capture. Reagents such as 7-chloro-4-nitrobenzyl-2-oxa-1,3-diazole and 1-dimethylaminonaphthalene-5-sulfonyl chloride are known for forming fluorescent derivatives of amines, thiols, and phenols. The class of organic compounds, their functional groups and some specific examples of reagents that may be used are given in Table 14.2.

TABLE 14.2
Functional Groups and Some Derivatizing Reagents

Functional Groups	Reagents for Derivatization
Carboxylic acid, –COOH	Methanol or any lower alcohol for acid-catalyzed esterification, for example, BF_3—methanol/butanol; diazomethane produces methylesters; benzyl bromide or pentafluorobenzyl bromide yield esters; dialkylacetals, for example, DMF-dimethylacetal, dibenzylacetal, for example, DMF-dibenzylacetal or diazoalkales used for acetylation/esterification of acids for GC or GC/MS analysis; reaction with 4-bromomethyl-7-methoxycoumarin produces fluorescent derivatives for HPLC analysis; O-4-nitrobenzyl-N,N-diisopropylisourea for UV absorption at 254 nm (HPLC); reactions with amines produce amide derivatives (for GC or GC/MS analysis); also acids can be converted into silyl derivatives for their analysis, using silylating reagent, such as, trimethylchlorosilane, bis(trimthylsilyl)acetamide, or trimethylsilylimidazole
Aldehyde and Ketone, >C=O	Reaction with 2,4-dinitrophenylhydrazine or semicarbazide for spectrophotometric, GC-NPD or GC/MS determination; 1-Dimethylaminonaphthalene-5-sulfonyl hydrazine for fluorescent-HPLC analysis: O-alkylhydroxylamines give O-alkyloximes, for example, pentafluorobenzylhydroxylamine hydrochloride in methanol forms pentafluorobenzyloxime derivatives
Alcohol, R–OH	Reactions with 3,5-dinitrobenzoyl chloride give derivatives for HPLC-UV analysis at 254 nm); reactions with carboxylic acids convert into esters (for GC or GC/MS analysis); other reagents include perfluoro acid anhydrides, fluorinated acylimidazoles, and N-methylbis(trifluoroacetamide) converting alcohols into their fluoroacyl derivatives; can form silyl derivatives with silylation reagents
Amines, R–NH_2	7-Chloro-4-nitrobenzyl-2-oxa-1,3-diazole or 1-dimethylaminonaphthalene-5-sulfonyl chloride forms fluorescent derivatives (HPLC analysis); perfluoroacid anhydrides, for example, trifluoroacetic anhydride or trifluoroacetylimidazole form corresponding acyl derivatives of amines for mass spectrometric analysis; other derivatization reagents for amines include TBH; acid anhydrides; acyl chlorides; acyl imidazoles; N-methylbis(trifluoroacetamide); and acyl amides; silyl derivatives can be prepared from bis(trimethylsilyl)acetamide, bis(dimethylsilyl)trifluoroacetamide, and pentafluorophenyldimethyl silyl reagents
Phenols, Ar–OH	Phenols and chlorophenols react with pentafluorobenzyl bromide forming their pentaflurobenzyl ethers that can be analyzed by GC-ECD or by GC/MS with negative ion chemical ionization; perfluoroacid anhydrides and fluorinatedacylimidazoles form perfluoroacyl compounds; chloronitrobenzyl oxadiazoles and dimethylaminonaphthalene-S-sulfonyl chloride form fluorescent derivatives that can be measured by HPLC-fluorescent detector
Thiols, R–SH	Dialkylacetals, for example, DMF-dimethyacetal form S-methyl derivatives; chloronitrobenzyloxazoles, and dimethylaminonaphthalene-S-sulfonyl chloride form fluorescent derivatives (HPLC); pentafluorobenzylbromide, and perfluoroacid anhydrides are among other derivatizing reagents; silyl derivatives can be made by reacting with trimethylchlorosilane and other silylation reagents

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15 Microbial Analysis

COLIFORM GROUPS OF BACTERIA

A variety of bacteria, parasites, and viruses, known as pathogens can potentially cause health problems in humans from ingestions. The sanitary quality of all waters for the purpose of drinking, bathing, swimming, or for wastewater treatments is mostly evaluated from coliform tests. Such microbial examinations serve as indicator of the quality of water supplies. The term "Coliform" broadly refers to all lactose fermenting, gas forming members of the family of bacteria, known as, *Enterobacteriaceae*. Such bacteria also include the intestinal microbes *Escherichia coli (E. coli)*, *Salmonella*, and *Enterbacter.* However, there may be many soil bacteria that also ferment lactose. Since it may not be feasible to test the presence of all fecal contaminating pathogens in the water, the presence of *E. coli* is used instead as an indicator organism to determine any possible fecal contamination.

Total coliforms (TCs) include a group of bacteria that generally are not harmful to humans. Coliform bacteria are not disease causing organisms. However, they are found to occur in small concentrations, associated with disease-causing microorganisms, known as pathogens that cause infectious waterborne diseases. The tests for TCs, therefore, are used as primary indicators to determine whether or not the water is suitable for drinking. Such tests also determine the adequacy of the water treatment process and integrity of the water distribution system. Coliform bacteria occur in the intestines of warm blooded mammals, including humans. They are found in soils and many surface waters, the primary source being human and animal wastes, and medical wastes. They are found in vegetation and other environmental matrices. The term TCs also include the fecal coliforms, a subgroup of bacteria that are present specifically in the gut and feces of warm-blooded animals. *E. coli* is a subgroup of fecal coliforms that are also harmless bacteria and exist in the intestines of humans and warm-blooded animals. Some strains, however, can cause illness. The presence of *E. coli* in the water may indicate recent fecal contaminations and thereby implying a risk of presence of pathogens in the water.

Bacteria, viruses, protozoa, helminthes, and other organisms can be analyzed by microbiological methods and also by molecular biology techniques. The microbial methods, however, are less expensive and provide quantitative (semiquantitative) results. Only microbial methods are discussed in this chapter. In these methods, the microbes are cultured under controlled conditions, and then microscopic measurements are used to detect and quantify them. Microbial methods provide quantitative results and are less expensive in comparison to molecular biology techniques.

There are several methods for testing microbial groups in water. Many such methods, though not sensitive, may however allow rapid detection of microbes. Such rapid detection may have very limited applications though, because the sensitivity of the testing may go down. Such special rapid techniques for microbial testing include the bioluminescence test for nonspecific microflora (the testing time is 1 h, the sensitivity of the test however is low, 100,000 cells/mL sample) and radiometric and colorimetric tests for fecal coliforms. The radiometric test is short and sensitive (the testing time is 4–5 h and a low coliform number, between 2 and 20 cells/mL may be measured). The fecal coliforms may also be determined by a "7 hours test" using a special medium. The test may not be accurate. All these methods are briefly outlined below. The tests for pathogens can be complex and time consuming, therefore TCs analysis, that are simple and less laborious may be performed in lieu of the more complex tests. Since TCs indicate the presence of other pathogens in drinking water, therefore their tests in the water is of paramount importance to determine the quality of drinking water and such test results must be negative, that is, coliforms must not be detected in the drinking

water. The maximum contaminant level goal (MCLG) for the TCs set by the US Environmental Protection Agency for drinking water is zero.

The microbiological analysis usually involves the following steps: (a) isolation of the microorganisms, typically by filtration through a microporous membrane (e.g., 0.45 μm cellulose ester) from an aqueous phase, (b) the membrane after filtration is placed on a selective medium and incubated under controlled conditions (at a defined temperature for a specific time) to allow the growth of the bacteria, (c) after incubation the filter is removed, and dried to fix the colonies on the membrane, (d) the membrane is placed in a solution containing a dye, (e) excess dye is removed by washing with a solvent, and (f) the filter is dried and the colonies are counted using a fluorescence microscope or a sensitive luminescence meter. (*Fluorescence Microscope*: This is an optical microscope which uses the phenomena of fluorescence and phosphorescence instead of, or in addition to, reflection and absorption. The organism of interest in the specimen is labeled with a fluorescent molecule or a dye. The specimen is illuminated with light of a specific wavelength (e.g., longer wavelength ultraviolet light) which is absorbed by the fluorophores, emitting visible light of longer wavelength.)

Some drawbacks of these methods, however, include the possibility of misidentification of organisms due to interference from many small and unknown spores, viruses, and bacteria. Also, these methods are very laborious and time consuming and require equally tedious quality control (QC) steps. These tests mostly use the agar medium. The temperature and the time set for incubation for the cells to grow depends on the type of microorganisms.

There are primarily two different microbial tests to determine TCs in the water. One is the *membrane filter (MF) method* and the other is *multiple tube fermentation method, also known as the most probable number or MPN test*. The conceptual approaches are different for these two methods. While the MF method involves separating bacteria by filtration, incubating them in growth enrichment media and counting the numbers of colonies, the MPN test involves setting up a series of dilutions and replicates and the carbon dioxide gas released from the growth of coliform bacteria is monitored and a statistical analysis is used to determine the MPN of bacteria in the sample. Both these methods are presented below. The MF method described below is the U.S. EPA Method 1604 to carry out the analysis of TCs and *E. coli* in water simultaneously.

SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Samples are collected in sterile polypropylene containers. Any residual chlorine in the sample should be neutralized by sodium thiosulfate solution at the time of sampling. Use 1 mL of 10% $Na_2S_2O_3$ solution per 1 L of sample. The holding time for the source sample should not exceed 6 h after collection and its analysis should be completed within 8 h. Drinking water samples however may be analyzed within 30 h. It is recommended that the sample should be analyzed as soon as possible after collection. The sample bottles should be placed in ice during their transit to the laboratory and placed in a refrigerator thereafter for storage at the temperature of 1–4°C.

MF METHOD FOR TESTING TCs AND *E. COLI*

Outline of the Method

The method here uses membrane infiltrating (MI) agar or MI broth. The purpose is to detect and quantify TCs and also *E. coli* at the same time in 24 h or less based on their specific enzyme activities. Two enzyme substrates are used in the medium. One is fluorogen, 4-Methylumbellifery-*beta*-D-pyranoside (MUGal) to detect the enzyme, beta-galactosidase produced by TC. The other enzyme substrate included in the medium is chromogen, indoxyl-*beta*-D-glucuronide (IBDG) to detect the enzyme, beta-glucuronidase produced by *E. coli*. A wide range of sample volumes or dilutions can be used in this method to detect and quantify TC and *E. coli* respectively over a wide range.

A measured volume of water, usually 100 mL, or an appropriate volume is filtered through a cellulose ester MF of 47-mm, 0.45-um pore size. The bacteria present in the sample is filtered and retained on the MF. The filter is placed on a 5-mL plate of MI agar or an adsorbent pad saturated with 2–3 mL of MI broth. The plate is then incubated for 24 h at 35°C. Bacteria colonies that grow on the plate produce a blue color from the breakdown of IBDG by the *E. coli* enzyme, *beta*-glucuronidase. The colonies that grow from the breakdown of MUGal by the TC enzyme, *beta*-galactosidase are inspected under fluorescence at long wavelength ultraviolet light at 366 nm. In other words, TCs are those bacteria that produce fluorescent colonies upon exposure to ultraviolet light at 366 nm after primary culturing on MI agar or broth. If the fluorescent colonies are of blue–white color this indicates the presence of TC other than *E. coli*. If the fluorescent colonies are blue-green in color or if there are fluorescent halos around the edges of the blue-green, this is attributed to *E. coli* colonies. Sometimes, though rarely, nonfluorescent blue colonies do also appear. In such a case, they are added to the count because the fluorescence is masked by the blue color from the breakdown of IBDG.

In this method, the *E. coli* are those bacteria that produce blue colonies under ambient light after culturing on MI agar or broth. These colonies under ultraviolet light at 366 nm can be fluorescent or nonfluorescent.

Interference

Colloidal or suspended particles in the water sample can clog the MF and mar filtration. Also such clogging may cause spreading of bacteria colonies. This could interfere in identifying target colonies.

Sometimes tiny and flat colonies of small size, below 0.5 mm diameter in low numbers (below 200 colonies) interfere in the *E. coli* test. If that happens, they should not be counted as *E. coli* colonies, which are relatively large in size, with diameter between 1 and 3 mm. In the absence of typical *E. coli*, these small-sized colonies are not observed. Also, bright green fluorescent colonies are occasionally observed along with the typical blue-white or blue-green TC colonies. They generally occur however in low numbers and can be identified distinctly from the TC colonies and should be excluded in the TC count.

Reagents, Standards, and Equipment

The equipment required to carry out analysis of coliforms bacteria are listed below.

An incubator set at 35 ± 0.5°C with approximately 90% humidity; a stereoscopic microscope, wide-field type with magnification of 10–15×; a microscope lamp; white fluorescent lamps adjusted to give maximum color; long wavelength ultraviolet lamp (366 nm); water bath for agar preparation; membrane filtration units, glass, plastic, or stainless steel; MFs, white grid marked, cellulose ester 47-mm diameter, 0.45-um pore size, presterile or sterilized for 10 min at 121°C, 15-lb pressure; a vacuum filter flask; vacuum source; thermometers, National Institute of Standards and Technology (NIST) certified; glass apparatus: pipets, graduated cylinders, bottles, and flasks of various sizes, sterilized; Petri dishes, plastic or glass, sterilized; test tubes with screw cap, borosilicate or plastic, sterilized; syringe, sterile, plastic, disposable; forceps.

The reagents and standards for all microbial tests should be of the highest grades of purity or microbiological grade, and certified. The preparations of phosphate-buffered solution, soy agar, and other reagents are outlined below. All solutions must be sterilized by filtration or autoclave for 15 min at 121°C at 15-lb pressure. The prepared solutions can be stored in a refrigerator until used. The solutions should be discarded if there is evidence of mold formation or contaminations. The reagents should be prepared fresh then.

Stock phosphate buffer solution is made by dissolving 34.0 g potassium dihydrogen phosphate (KH_2PO_4) in 500 mL reagent-grade distilled water. The pH of this solution is adjusted to 7.2 with

1 N NaOH. The final volume of this solution is adjusted to 1 L with reagent grade distilled water and sterilized.

Magnesium chloride solution is made by dissolving 38 g anhydrous $MgCl_2$ or 81.1 g of hydrated $MgCl_2$ ($MgCl_2 \cdot 6H_2O$) in 1 L of reagent grade distilled water and sterilized.

Working solution: The final pH of the solution should be 7.0 ± 0.2. It is made by adding 1.25 mL phosphate buffer and 5 mL $MgCl_2$ stock solutions for each 1 L of reagent-grade distilled water and mixed well and sterilized.

MI agar should have the following compositions in 1 L reagent-grade water: proteose peptone # 3, 5.0 g; yeast extract 3.0 g; beta-D-lactose 1.0 g; 4-methylumbelliferyl-beta-D-galactopyranoside (MUGal) 0.1 g; IBDG 0.32 g; sodium chloride (NaCl) 7.5 g; dipotassium hydrogen phosphate (K_2HPO_4) 3.3 g; potassium dihydrogen phosphate (KH_2PO_4) 1.0 g; sodium lauryl sulfate 0.2 g; sodium desoxycholate 0.1 g; and agar 15.0 g. All these compounds in above amounts should be dissolved in 1 L of reagent-grade distilled water. The final concentration of MUGal in the above solution should be 100 ug/mL, and IBDG 320 ug/mL. Prepare cefsulodin solution (1 mg/mL) by adding 0.02 g cefsulodin to 20 mL reagent-grade distilled water and then sterilize using 0.22-um syringe filter. This solution should be stored in a sterile tube at 4°C. Fresh solution should be made each time.

Preparation of the MI agar: Autoclave the agar medium (prepared above) for 15 min at 121°C and 15-lb pressure. Add 5 mL of the freshly prepared solution of cefsulodin (5 mL/L of agar medium, which would make the final concentration of cefsulodin in the medium, 5 ug/mL). Pipet the medium into 9×50 mm Petri dishes (5 mL/plate). The final pH should be 6.95 ± 0.2. Store the plates at 4°C for up to 2 weeks.

Preparation of MI broth: MI broth is prepared in the same way as MI agar, however, without the agar. Thus, the compositions of all ingredients remain the same, except that no agar is added here. The final pH of the MI broth should be 7.05 ± 0.2. The broth is sterilized in the same way. Absorbents pads are placed in Petri dishes (9×50 mm) and saturated with 2–3 mL of MI broth containing 5 ug/mL final concentration of cefsulodin. The broth can alternatively be filter-sterilized. Excess broth is poured off before using plates. The plates should be stored in the refrigerated and discarded after 4 days.

Tryptic soy agar/trypticase soy agar (TSA): The composition of this soy agar is: tryptone 15.0 g; soytone 5.0 g; sodium chloride (NaCl) 5.0 g; and agar 15.0 g. All the dry reagents above are added to 1 L of reagent-grade distilled water. The solution is heated to boiling to dissolve the agar completely. The solution is then autoclaved for 15 min at 121°C at 15-lb pressure. Transfer the agar solution into 9×50-mm Petri dishes, 5 mL/plate. Incubate the plates for 24–48 h to check for contamination. Discard any plates with growth. Discard all plates if >5% of the plates show contamination and prepare new medium. The final pH should be 7.3 ± 0.2. Store at 4°C.

Quality Control

The QC steps should be adhered strictly to prevent any growth from cross contamination and reporting of wrong results. The QC steps are discussed in detail in all the literature on the coliform tests. As mentioned before, all reagents and standards used must comply with the requirements of microbiological analysis. Each batch of MI agar or broth must be pretested for its performance, such as to ensure if correct enzyme reactions are occurring with known cultures. New lots of MFs should be tested against an acceptable reference lot. Specific filtration control tests should be performed each time samples are analyzed.

Control tests must be carried out for MFs, phosphate-buffered dilution waters, and also for the MI agar or broth. In all these tests, the absence of growth should indicate that the reagents and standards are free from any contamination and the test results are reliable and meet the acceptance criteria. For the filter control test, place one or more MFs on TSA plates and incubate for 24 h at

35°C. For the phosphate-buffered dilution water control test filter a 50-mL volume each of sterile dilution water before beginning the sample filtrations and after the completion of filtrations. Place the filters on TSA plates and incubate the plates for 24 h at 35°C. Similarly perform a QC control test for agar or broth. For this, place one or more TSA plates and one or more MI agar plates or MI broth pad plates in the incubator for 24 h at 35°C. Broth pad plates should be incubated grid-side up and not inverted like the agar plates. Absence of growth in all these tests should indicate the sterility of the filters, the dilution water, and the plates, respectively.

Procedure

The prepared MI agar or MI broth and the TSA plates stored in a refrigerator are allowed to warm to room temperature before testing. Label all the plates at the bottom with the sample numbers and also the QC control plates. Using a forceps, place the MF on the porous plate of the filter base. Place the grid side up.

Attach the funnel to the base of the filter unit. The MF is now placed between the funnel and the base. Pour approximately 30 mL of sterile dilution water in the bottom of the funnel. Shake the sample container vigorously several times.

Measure 100 mL of drinking water with a sterile pipette or graduated cylinder and transfer into the funnel. Alternatively use an appropriate volume or diluted sample for the tests. Turn on the vacuum and rinse the funnel twice with 30 mL sterile dilution water. Remove the funnel from the base of the filter unit. Sanitize the funnel between filtrations using a germicidal ultraviolet (254 nm) light box with 2-min exposure for decontamination.

Holding the MF at its edge with flamed forceps gently lift and place the filter grid side up on the MI agar plate or MI broth agar pad plate. Slide the filter onto the agar or pad. Avoid trapping air bubbles between the MF and the underlying agar or absorbent pad. The filter must make contact with the agar or pad.

Invert the agar Petri dish and incubate the plate at 35°C for 24 h. Pad plates used with MI broth should be incubated grid side up. The plates should be placed in a humid chamber if loose-lidded plates are used.

Count all blue colonies on each MI plate under normal or ambient light and record the results. This is the *E. coli* count. Positive results that occur in less than 24 h are valid. Results can be recorded as negative only after the completion of the 24 h incubation period.

Now expose each MI plate to longer wavelength ultraviolet light at 366 n. Count all fluorescent colonies. Blue/green fluorescent are *E. coli* colonies. Blue/green with fluorescent edges are also *E. coli* colonies. Blue/green fluorescent colonies are TCs without *E. coli*. If any blue nonfluorescent colonies are found on the same plate, this should be added to the TC count.

Calculations/Data Analysis

The following general rules may be used to calculate the *E. coli* and TC per 100 mL sample. Select and count filters with <200 total colonies per plate. Select and count filters with less than 100 target colonies. If the total number of colonies is too numerous to count or confluent, then record the results for TC^+ as (TNTC) and count the number of *E. coli*. If both the target organisms are greater than 200, record the results as "TC^+ EC^+ (TNTC)."

Calculate the final values from the following formula:

$$\textit{E. coli}/100\,\text{mL} = (\text{Number of blue colonies/volume of sample filtered, mL}) \times 100$$

$$\text{TC}/100\,\text{mL} = [(\text{Number of fluorescent colonies}) + (\text{Number of blue nonfluorescent colonies, if any})/(\text{Volume of sample filtered, mL})] \times 100$$

MULTIPLE TUBE FERMENTATION/MPN INDEX TEST

While the MF method is a direct plating method that permits a direct count of coliform colonies, the multiple tube fermentation technique or the MPN index test on the contrary are not actual enumerations of coliform count. In this technique, multiple tubes are used to observe fermentation. Sample aliquots at different dilutions are inoculated and the number of positive tubes is counted for the growth of colonies. The results of the tests of such replicate analyses and their dilutions are expressed in terms of the MPNs of organisms present in the sample. Thus, in the MPN test, the number determined is an estimate of mean density of coliforms in the water and is based on certain probability formulas. In most routine analyses, tables are used to read the estimate number of colonies. Such tables are based on the assumption of a random or Poisson distribution. The test results as in the MF method are expressed as the number of colonies per 100 mL of water. The precision of the multiple tubes fermentation test depends on the number of tubes used. The results of the test are reliably assessed when the largest sample inoculums examined show gas bubbles either in all tubes or in most of the tubes while the smallest inoculums of samples shows no gas in all tubes (or in a majority of the tubes). The TCs in the sample by the MPN test may also be calculated from Thomas' formula given below, instead of reading from the reference MPN tables:

$$\text{MPN}/100\,\text{mL} = (\text{Number of positive tubes} \times 100)/[(\text{mL sample in negative tubes}) \times (\text{mL sample in all tubes})]^{1/2}$$

Outline of the Test

The test consists of essentially three steps: the presumptive, confirmed, and completed tests. All materials used for containing or transferring samples must be sterile and the work area must be disinfected. Mix the sample thoroughly before carrying out the test. In the presumptive test, a moderately selective lactose broth medium, lactose lauryl tryptose (LT) broth is used. If the presumptive test is positive, then use brilliant green bile (BGB) broth to confirm if the sample has TCs. If the test for the TCs shows positive result then only proceed to test for the fecal coliforms and *E. coli*. For the fecal coliforms test, use *E. coli* medium broth tubes and for the *E. coli*, use *E. coli* medium with MUG. The number of tubes for use in the MPN test may vary, though a 10-tube test is common. A 5-tube test may alternatively be carried out to save time. The MPN test procedure is briefly highlighted below.

Procedure

For the presumptive test, transfer 10 mL of sample using a sterile pipet into each of the 10 (or 5) tubes of LT broth. Tighten the screw cap on each tube after adding the sample. Invert and swirl the tubes several times to mix the sample thoroughly with the nutrient medium. Make sure the inner vial in each tube is full of liquid with no air bubble present. Place the tubes in an incubator at a temperature of 35°C. After 1 h, invert the tubes to remove trapped air in the inner vials. Any bubble that forms in 1 h is not from bacteria. Remove the bubbles if seen during this period and then carefully return the tubes to an upright position.

Continue incubation. After 24 h, examine the inner vial of each tube for gas. If the broth becomes cloudy and the inner vials contain gas bubbles, coliform bacteria are likely to be present. If no gas bubble is seen in the inner tubes, incubate again for another 24 h. Examine the inner vials again after this period. Any gas bubble in the inner vials would indicate the presence of coliform bacteria in the sample. Count the number of tubes that contain the gas bubbles. This is presumptive test to determine the TC in the sample.

If the sample contains coliform, then perform a confirmed test for all tubes that contain gas. The test will eliminate any false positive results from the above presumptive test. Use BGB broth for this confirmation test. Use a sterile disposable loop for all inoculations. Put the loop into the positive LT broth tubes that contained gas bubbles and then into the BGB broth tube. Replace and tighten the screw cap on each tube immediately, invert and swirl the tubes. Vent out any trapped air from the inner vials. Incubate the BGB tubes for 24 h at 35°C and examine the inner vials for any gas formation. If no gas is seen, continue incubation for another 24 h. If the inner vial contains gas after this period, the test is positive for TC bacteria. If none of the tube contains gas, no coliform is present in the sample.

If the confirmation test shows TC, then complete the test for fecal coliform and *E. coli* bacteria. Use *E. coli* medium broth for fecal coliform test. Use 10 or 5 tubes like before and inoculate the *E. coli* medium broth from each positive LT broth tube using a sterile loop. Incubate at 44.5°C for 24 h and examine inner vials for any gas formation. If no gas is seen, the test is then negative for fecal coliform. If gas bubble is observed, count the number of tubes that contain the gas to determine fecal coliform and refer to the MPN table.

Now to determine *E. coli*, use *E. coli* medium with MUG broth tubes. The procedure otherwise is much the same as above for the fecal coliform. That is, from each positive LT broth tube inoculate with a loop the *E. coli* medium with MUG broth and incubate for 24 h at 44.5°C. The formation of gas bubbles in the inner vial would indicate the presence of *E. coli*. Count the number of tubes and refer to the MPN table to determine *E. coli* in the sample.

RADIOMETRIC DETECTION OF FECAL COLIFORMS

The technique permits presumptive detection of less than 20 coliform bacteria (between 2–20 cells) in 4–5 h testing time. In this test, a Carbon-14 radioactive substrate, namely, ^{14}C—mannitol is uniformly labeled onto the M-FC broth. The incubation is carried out at two temperatures, first at 35°C for 2 h and then at 44.5°C for 2.5 h. The labeled substrate is added at the start of the second incubation period, 44.5°C. Membrane filtration is carried out to concentrate organisms from the sample. The MF is placed in M-FC broth in a sealed tube. The radioactive $^{14}CO_2$ released by the fecal coliforms is trapped on a filter paper disc saturated with $Ba(OH)_2$ solution. The C-14 radioactivity is assayed by liquid scintillation spectrometry.

BIOLUMINESCENCE TEST

The bioluminescence test, also known as "Firefly Luciferase Test" measures the adenosine triphosphate (ATP) in living cells. The reaction occurs between the luciferase enzyme, luciferin, magnesium ions, and ATP (extracted from living cells) emitting light. The light is measured quantitatively. The light emitted is quantitatively related to the quantity of ATP extracted, and therefore to the number of bacteria. ATP is the limiting reactant in the reaction and all other reactants except ATP are taken in excess. Addition of ATP drives the reaction producing pulse of light that is quantified and that is proportional to the concentration of ATP, and thereby to the number of bacteria in the sample. Low concentration of bacteria in the sample can be measured by concentrating the bacteria by the membrane filtration technique and using a larger volume of sample, usually 1 L. The assay is completed in less than 1 h.

SEVEN-HOUR FECAL COLIFORM TEST

This test is similar to the MF procedure for fecal coliforms except that a different medium, M-7h FC agar, is used and the incubation temperature is 41.5°C. An appropriate volume of sample is filtered through a MF. The filter is placed on the surface of a plate containing the agar medium for 7 h at 41.5°C. Lactose fermentation is indicated from yellow fecal colonies.

The medium should be prepared in dehydrated form. The ingredients are polypeptone, yeast extract, lactose, d-mannitol, sodium chloride, sodium lauryl sulfate, sodium desoxycholate, bromocresol purple, phenol red, and agar. The mixture is dissolved in hot distilled water at 60°C, pH adjusted to 7.3, cooled to 45°C, and a few mL of the solution is dispensed to petri plates for the test. The prepared medium may be stored for 30 days if refrigerated.

Section II

Specific Classes of Substances and Aggregate Properties

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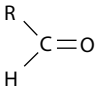
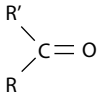
16 Aldehydes and Ketones

Aldehydes and ketones constitute an important class of organic compounds containing the carbonyl group. An aldehyde has the structure RCH(=O) while a ketone has the structure $R_2C(=O)$.



(Aldehyde)



(Ketone)

where R may be an alkyl, alkenyl, alkynyl, or aryl group. In aldehyde, one hydrogen atom is attached to the carbonyl group, while in ketone no hydrogen is bound to the carbonyl group. In formaldehyde, two hydrogen atoms are bound to the carbonyl group. Thus, aldehydes and ketones are compounds of closely related classes exhibiting many similar chemical properties.

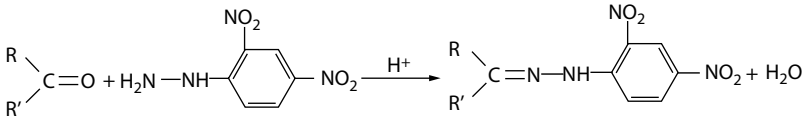
Low molecular weight aldehydes and ketones are used in the manufacture of resins, dyes, esters, and other organic chemicals. Many ketones including acetone and methyl ethyl ketone (MEK) are industrial solvents. Some of the compounds that are used commercially are presented in Table 16.1. Many aldehydes and ketones are emitted into the atmosphere from chemical and combustion processes. The photochemical degradation of many organic substances also generates lower aldehydes and ketones.

Aldehydes and ketones of low molecular weights are volatile compounds and can be extracted from the sample matrix by purge and trap or the thermal desorption technique, and determined by GC-FID or GC/MS. Compounds of low carbon numbers ($R < 4$) are soluble in water causing poor purging efficiency and, therefore, producing elevated detection levels. Therefore, heating of the purging vessel may become necessary to enhance the purging efficiency of such compounds. Alternatively, aqueous samples may be directly injected onto the GC column for separation and detection by an FID. This also gives a higher detection level. Two alternative methods may be used to analyze these compounds more accurately with a lower detection level. These methods are based on derivatization with 2,4-dinitrophenylhydrazine (DNPH) and the determination of the derivatives by (1) GC using a nitrogen-specific detector (NPD) (i.e., NPD in N-specific mode) and (2) reverse phase HPLC using a UV detector.

The basic techniques for the determination of aldehydes and ketones are summarized in Figure 16.1.

DERIVATIZATION WITH 2,4-DNPH

The carbonyl group of an aldehyde or a ketone reacts with DNPH to form a stable derivative according to the following equation:



(Ketone) (DNPH) (DNPH-derivative)

DNPH is often susceptible to formaldehyde or acetone contamination. Therefore, it should be crystallized with acetonitrile to remove any impurities. Repeated crystallization may further be

TABLE 16.1
Some Commercially Used Aldehydes and Ketones

CAS No.	Compounds	Synonyms
	Aldehydes	
[75-07-0]	Acetaldehyde	Ethanal
[107-02-8]	Acrolein	2-Propenal
[100-52-7]	Benzaldehyde	Benzoic aldehyde
[123-72-8]	Butyraldehyde	Butanal
[104-55-2]	Cinnamaldehyde	3-Phenyl-2-propenal
[123-73-9]	Crotonaldehyde	2-Butenal
[112-31-2]	Decyl aldehyde	Decanal
[5779-94-2]	2,5-Dimethylbenzaldehyde	–
[50-00-0]	Formaldehyde	Methanal
[107-22-2]	Glyoxal	Ethanedial
[111-30-8]	Glutaraldehyde	1,5-Pentanedial
[111-71-7]	Heptaldehyde	Heptanal
[66-25-1]	Hexaldehyde	Hexanal
[78-84-2]	Isobutyraldehyde	Isobutanal
[590-86-3]	Isovaleraldehyde	3-Methylbutanal
[78-85-3]	Methacrolein	Isobutenal
[18829-56-6]	Nonenaldehyde	2-Nonenal
[124-13-0]	Octaldehyde	Octanal
[123-38-6]	Propionaldehyde	Propanal
[620-23-5]	*m*-Tolualdehyde	3-Methylbenzaldehyde
[529-20-4]	*o*-Tolualdehyde	2-Methylbenzaldehyde
[104-87-0]	*p*-Tolualdehyde	4-Methylbenzaldehyde
[110-62-3]	Valeraldehyde	Pentanal
	Ketones	
[67-64-1]	Acetone	2-Propanone
[123-54-6]	Acetyl acetone	2,4-Pentanedione
[108-94-1]	Cyclohexanone	Cyclohexylketone
[120-92-3]	Cyclopentanone	Ketocyclopentane
[96-22-0]	Diethyl ketone	3-Pentanone
[108-83-8]	Diisobutyl ketone	Isovalerone
[123-19-3]	Dipropyl ketone	4-Heptanone
[541-85-5]	Ethyl amyl ketone	5-Methyl-3-heptanone
[106-35-4]	Ethyl butyl ketone	3-Heptanone
[591-78-6]	Methyl butyl ketone	2-Hexanone
[78-93-3]	MEK	2-Butanone
[110-12-3]	Methyl isoamyl ketone	5-Methyl-2-hexanone
[141-79-7]	Methyl isobutenyl ketone	Mesityl oxide
[108-10-1]	Methyl isobutyl ketone	4-Methyl-2-pentanone
[563-80-4]	Methyl isopropyl ketone	3-Methyl-2-butanone
[107-87-9]	Methyl propyl ketone	2-Pentanone

performed to achieve the desired level of purity for DNPH. A 100 mL aliquot of aqueous sample is buffered with a citrate buffer and the pH is adjusted to 3 ± 0.1 with HCl or NaOH. The acidified sample is then treated with the DNPH reagent and heated at 40°C for an hour under gentle swirling. The DNPH derivatives of aldehydes and ketones formed according to the above reaction are

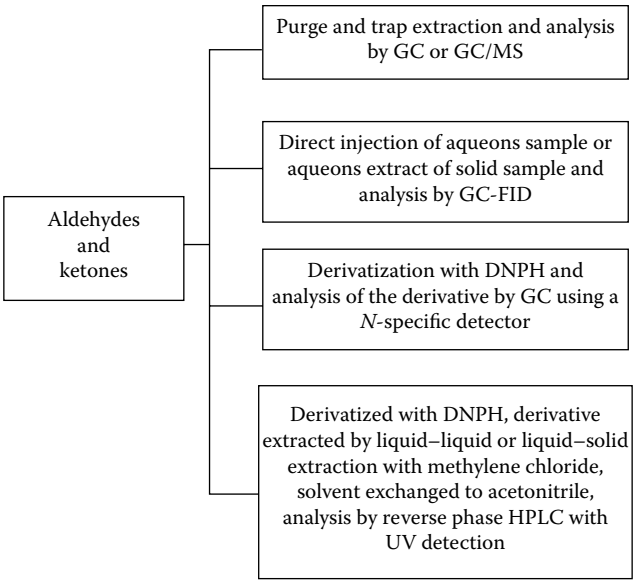


FIGURE 16.1 Schematic representation of the basic techniques for determining aldehydes and ketones.

extracted with methylene chloride using LLE. The extract is then solvent exchanged to acetonitrile for HPLC determination.

The DNPH derivatives may also be extracted by solid-phase extraction (liquid–solid extraction [LSE]). The sorbent cartridge is conditioned with 10 mL of dilute 1 M citrate buffer solution (1:25 dilution) and 10 mL of saturated NaCl solution. The cartridge is then loaded with the extract and the derivatives eluted with acetonitrile.

If formaldehyde is the only compound to be analyzed, an acetate buffer may be used instead of a citrate buffer, and the sample may be pH adjusted to 5 ± 0.1.

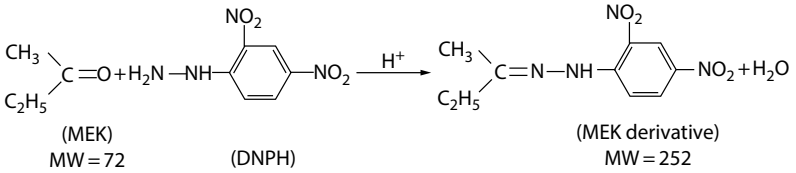
Soils, sediments, and solid wastes may be extracted with the extraction fluid (sample to fluid mass ratio 1:20) in a rotating bottle at approximately 30 rpm for 18 h. The extraction fluid is made from the citrate buffer and pH adjusted to 3 ± 0.1 for DNPH derivatization. The derivatives are extracted with methylene chloride.

If the compounds are derivatized with DNPH and the derivatives are determined by GC or HPLC, the equivalent concentrations of the parent carbonyl compounds in the sample may be stoichiometrically determined as shown below in the following example.

EXAMPLE 16.1

A 200-mL aliquot of an aqueous sample was pH buffered and derivatized with DNPH. The DNPH derivatives were extracted with methylene chloride and the extract was solvent exchanged to 50 mL acetonitrile. Analysis by HPLC–UV showed the presence of MEK derivative that was quantitated as 2.7 mg/L in the extract, using the calibration standards prepared from the solid derivative. Determine the concentration of the MEK in the sample.

The derivatization reaction is as follows:



The concentration of MEK derivative in 50 mL acetonitrile extract = 2.7 mg/L, which is equivalent to

$$\frac{2.7 \text{ mg MEK derivative}}{1\text{L extract}} \times \frac{72 \text{ g}}{252 \text{ g MEK derivative}}$$

or 0.77 mg MEK/L extract solution.
Therefore, the concentration of MEK in the sample

$$= \frac{0.77 \text{ mg MEK}}{1000 \text{ mL extract}} \times \frac{50 \text{ mL extract}}{200 \text{ mL sample}} \times \frac{1000 \text{ mL sample}}{1\text{L sample}}$$
$$= 0.19 \text{ mg MEK/L}$$

Chromatographic Columns and Conditions

HPLC column: C-18 reverse phase column, such as Zorbax ODS or equivalent.
Mobile phase: acetonitrile/water (70:30) to 100% acetonitrile in 15 min.
Flow rate: ~1 mL/min.
Detector: Ultraviolet, set at 360 nm.
Sample injection: 25 μL.
GC column: aldehydes and ketones are polar compounds that can be separated on a polar or an intermediate polar column. Polyethylene glycol (PEG)-type phase, such as Carbowax 20 M, Supelcowax 10, VOCOL, DBWax, or equivalent is suitable for the purpose. Compounds may also be separated according to their boiling points on a nonpolar column. A 60 m long, 0.53 mm ID and 1 μm film or other appropriately dimensioned methyl silicone capillary columns, such as SPB-1, DB-1, or DB-5.

Sample Collection and Holding Time

Aldehydes and ketones are readily oxidized and must, therefore, be derivatized and extracted within 48 h of sample collection. The derivatized sample extracts should be analyzed within 3 days after preparation. Holding times exceeding more than 3 days have shown significant losses of compounds having seven or more C atoms. Samples should be collected without headspace and should be refrigerated and analyzed as soon as possible. Low molecular weight compounds may be stored for more than 3 days, but the analysis must be done within 7 days of sample collection.

AIR ANALYSIS

Aldehydes and ketones in ambient air may be determined by the U.S. EPA Method TO-5 or TO-11 or different NIOSH methods as listed in Appendices J and K. The EPA methods are based on derivatization of these carbonyl compounds in air with the DNPH reagent and measuring the stable DNPH derivatives (2,4-dinitrophenylhydrazones) by reverse phase HPLC with UV detection. Air is drawn through a midget impinger containing 2 N HCl solution of 0.05% DNPH reagent and isooctane. The derivatives formed are soluble in isooctane and dissolve into the organic layer. The aqueous layer is separated and extracted with hexane/methylene chloride (70:30). The extract is combined with isooctane and the three solvent mixtures are evaporated to dryness under a stream of nitrogen. The residue is dissolved in methanol and analyzed by HPLC.

The flow rate of air should be between 100 and 1000 mL/min, and not greater than 1000 mL/min. We recommend a sample volume of 40 L and an airflow of 400 mL/min. A volume of 10 mL each of DNPH reagent and isooctane should be used in the impinger. However, a larger volume,

20–25 mL isooctane would be suitable for a higher flow rate, ensuring that the solvent does not evaporate out during the process of sampling.

An alternative method suitable for formaldehyde and other aldehydes and ketones as well involves the use of DNPH-coated silica gel adsorbent (U.S. EPA Method TO5) instead of the reagent solution taken in an impinger. A known volume of air is drawn through a prepacked silica gel cartridge coated with acidified DNPH. Florisil (magnesium silicate) 60–80 mesh may be used instead of silica gel. The flow rate may be between 500 and 1000 mL/min. Sample volume and sampling time should be selected based on the expected range of concentration of the pollutants in the air or their time-weighted average values. The DNPH derivatives of the analytes are eluted from the adsorbent with acetonitrile for HPLC determination.

The column and conditions for HPLC analysis were outlined earlier in this chapter. If isomeric aldehydes or ketones coelute, alternate HPLC columns or mobile phase composition should be used. The DNPH reagent solutions should be always freshly prepared. Calibration standards should be made in methanol from solid DNPH derivatives. Intermediate standards should be prepared according to the anticipated levels for each component.

NIOSH Methods 1300 and 1301 (NIOSH, 1984) describe the determination of common ketones in air. The compounds evaluated in the study include acetone, methyl propyl ketone, methyl isobutyl ketone, methyl *n*-butyl ketone, diisobutyl ketone, cyclohexanone, ethyl butyl ketone, methyl amyl ketone, ethyl amyl ketone, mesityl oxide, and camphor [76-22-2]. The analysis involves adsorption of compounds over coconut shell charcoal, desorption with CS_2, and determination by GC-FID. The addition of a small amount of methanol (1%) into CS_2 gives a better desorption for some of the ketones. A volume of 10 L air at a flow rate of 100 mL/min may be sampled for the analysis. Many other ketones (not listed above) may be analyzed in a similar manner. Ambersorb XE-347 is an effective adsorbent for MEK (Method 2500, NIOSH, 1984).

Simple aldehydes, such as formaldehyde or acrolein may be analyzed by derivatizing into a suitable derivative for GC-FID or GC-NPD determination (Methods 2502, 2501, NIOSH 1984). The derivatizing agents for these compounds are 2-(benzylamino)ethanol and 2-(hydroxymethyl)piperidine, respectively, coated on a support. Formaldehyde may also be determined using colorimetry and polarography (Methods 3500 and 3501, NIOSH, 1984) (see Section III).

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17 Alkalinity

Alkalinity of water is a measure of its acid-neutralizing ability. The titrable bases that contribute to the total alkalinity of a sample are generally the hydroxides, carbonates, and bicarbonates. However, other bases such as phosphates, borates, and silicates can also contribute to the total alkalinity. The alkalinity value depends on the pH end point designated in the titration. The two end points commonly fixed in the determination of alkalinity are the pH 8.3 and pH 4.5 (or between 4.3 and 4.9, depending on the test conditions). When the alkalinity is determined to pH 8.3, it is termed *phenolphthalein alkalinity*. In such alkalinity titration, phenolphthalein or metacresol purple may be used as an indicator. On the other hand, the *total alkalinity* is measured by titrating the sample to pH 4.5 using bromocresol green as the indicator. Alkalinity may also be determined by potentiometric titration to the preselected pH. An acid standard solution, usually 0.02 N H_2SO_4 or HCl, is used in all titrations.

The procedure for potentiometric titration is presented in Chapter 6. In this titration, a standard acid titrant is added to a measured volume of sample aliquot in small increments of 0.5 mL or less, that would cause a change in pH of 0.2 unit or less per increment. The solution is stirred after each addition and the pH is recorded when a constant reading is obtained. A titration curve is constructed, plotting pH versus cumulative volume titrant added. The volume of titrant required to produce the specific pH is read from the titration curve.

CALCULATION

$$\text{Alkalinity, mg } CaCO_3/L = \frac{V \times N \times 50{,}000}{\text{mL sample}}$$

where

V is mL standard acid titrant used
N is normality of the standard acid

Since the equivalent weight of $CaCO_3$ is 50, the milligram equivalent is 50,000. Therefore, the result is multiplied by the factor of 50,000 to express the alkalinity as mg $CaCO_3$/L.

Alkalinity of a sample is essentially caused by the presence of three principal ions: hydroxide (OH^-), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-). The contribution of each of these ions may be determined from the following relationship:

Hydroxide alkalinity. When $P = T$, all alkalinity is due to OH^-, that is, hydroxide alkalinity is T. Also, when $P > 1/2\ T$ (but $< T$), hydroxide alkalinity is $2P - T$.
Carbonate alkalinity. When P is $1/2\ T$ or less (but >0), carbonate alkalinity is equal to $2P$, on the other hand, when $P > 1/2\ T$, the alkalinity due to $CO_3^{2-} = 2(T - P)$.
Bicarbonate alkalinity. When $P = 0$, there is no OH^- or CO_3^{2-} in the solution. The total alkalinity measured is all due to HCO_3^-. Thus, bicarbonate alkalinity $= T$.

When P is not 0, but $< 1/2\ T$, alkalinity due to $HCO_3^- = \left(T - 2P\right)$.

The alkalinity relationship may be directly read from a set of chart diagrams called nomographs, which are available from The American Water Works Association. Nomographical computations require that the following be known: the temperature, the pH, total dissolved solids, and the total alkalinity of the samples.

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18 Bromide

Bromide (Br^-) is the anion of the halogen bromine, containing an extra electron. It is produced from the dissociation of bromide salts in water. It may occur in ground and surface waters as a result of industrial discharges or seawater intrusion.

Bromide in water may be analyzed by one of the following three methods:

1. Phenol red colorimetric method
2. Titrimetric method
3. Ion chromatography

While the first method is used for low-level detection of bromide in the range of 0.1–1 mg/L, the concentration range for the titrimetric method is between 2 and 20 mg/L. The samples may be diluted appropriately to determine bromide concentrations at a higher range. Ion chromatography is used to analyze many anions including bromide and is discussed in Chapter 11.

PHENOL RED COLORIMETRIC METHOD

The bromide ion reacts with a dilute solution of sodium *p*-toluenesulfonchloramide (chloramine-T) and is oxidized to bromine that readily reacts with phenol red at pH 4.5–4.7. The bromination reaction with phenol red produces a color that ranges from red to violet, depending on the concentration of the bromide ion. An acetate buffer solution is used to maintain the pH between 4.5 and 4.7. The presence of high concentration of chloride ions in the sample may seriously interfere in the test. In such cases, the addition of chloride to the pH buffer solution or the dilution of the sample may reduce such interference effect. Remove free chlorine in the sample by adding $Na_2S_2O_3$ solution. In addition, the presence of oxidizing and reducing agents in the sample may interfere in the test.

Procedure

A 50 mL sample aliquot is treated with 2 mL buffer solution followed by 2 mL phenol red indicator and 0.5 mL chloramine-T solution. Shake well after each addition. Allow it to stand for 20 min. Add immediately 0.5 mL of sodium thiosulfate solution. Determine the concentration of bromide as mg/L from a calibration curve made by plotting bromide standards against absorbance at 590 nm. The color developed may also be compared visually in Nessler tubes against the bromide standards.

If the bromide concentration is too high, dilute the sample to a final concentration range of 0.1–1.0 mg Br^-/L. Multiply the results with dilution factor, if any.

Reagents

- pH buffer solution (pH 4.6–4.7): dissolve 6.8 g sodium acetate trihydrate, $CH_3COONa \cdot 3H_2O$, and 9.0 g NaCl in distilled water. Add 3.0 mL glacial acetic acid and make the volume to 100 mL.
- Chloramine-T solution: 500 mg in 100 mL distilled water.
- Phenol red indicator solution: 20 mg in 100 mL distilled water.
- Sodium thiosulfate solution: a 2 M solution is suitable. Dissolve 31.6 g anhydrous $Na_2S_2O_3$ or 49.6 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 100 mL.

- Bromide standards: anhydrous KBr, 0.7446 g is dissolved in distilled water and the final volume is made to 1 L (1.0 mL + 500 mg bromide).
- Dilute 10 mL of stock solution to 1 L to prepare secondary standard (1.0 mL + 5 μg Br^-) from which working standards are made. Dilute 0, 2, 5, 10, 15, and 20 mL of the above secondary standard to 100 mL with distilled water to obtain working standard solutions of 0, 0.1, 0.25, 0.5, 0.75, and 1.0 mg Br^-/L.

TITRIMETRIC METHOD

This titrimetric procedure (EPA Method 320.1) is similar to that of iodide. The sample is divided into two aliquots: one aliquot is analyzed for bromide plus iodide while the other aliquot is analyzed for iodide only. The difference of these two gives the concentration of bromide in the sample.

The sample is stored at 4°C and analyzed as soon as possible. Before analysis, the sample is pretreated with calcium oxide (CaO) to remove the interference effects of iron, manganese, and organic matter.

Determination of Bromide Plus Iodide

Bromide and iodide are oxidized to bromate (BrO_3^-) and iodate (IO_3^-) by treatment with calcium oxychloride [$Ca(OCl)_2$]. The reactions are as follows:

$$Br^- + 3Ca(OCl)_2 \rightarrow BrO_3^- + 3CaCl_2$$
$$I^- + 3Ca(OCl)_2 \rightarrow IO_3^- + 3CaCl_2$$

The so formed bromate and iodate react with I^- (obtained from the dissociation of KI) in acid medium, liberating iodine, as shown below in the following equation:

$$BrO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Br^- + 3H_2O$$
$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

The liberated iodine is titrated against standard sodium thiosulfate or PAO using starch indicator (see Chapter 6).

Procedure

Add 5–10 g CaO to 500 mL of sample. Shake vigorously and filter. Discard the first 100 mL of the filtrate.

In 100 mL aliquot of the above filtrate, dissolve 5 g of NaCl with stirring. Add HCl solution dropwise to adjust the pH to approximately 7 or slightly less. A pH meter should be used to measure the pH. Transfer the sample to a 250-mL iodine flask or a wide mouth conical flask.

Add 20 mL of 3.5% (m/v) calcium hypochlorite solution followed by 1 mL of 1:4 HCl solution. Add 0.2–0.3 g powdered $CaCO_3$. Heat the solution to boiling. Add 4 mL sodium formate solution (50% w/w) slowly. Heat to boiling for 10 min and occasionally wash down the sides with distilled water.

Allow the solution to cool. If precipitate forms due to iron, add potassium fluoride dihydrate. Add a few drops of sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) solution (1%).

Dissolve 1 g of KI in the above solution. Add 10 mL of 1:4 H_2SO_4. Allow the solution to stand in the dark for 5 min. Titrate this solution with standardized sodium thiosulfate or PAO solution, using

a starch indicator. Add the indicator when the solution becomes pale straw following the addition of $Na_2S_2O_3$ or PAO. At the end point, the blue color disappears. Disregard any reappearance of blue color. Run a distilled water blank.

Determination of Iodide

The titrimetric analysis of iodide is discussed in detail in Chapter 6.

Calculation

$$Br^-(mg/L) = (\text{Concentration of bromide} + \text{iodide}) - (\text{Concentration of iodide})$$

As shown in the equation above, the overall stoichiometry of the bromide reaction is

$$1\,\text{mol } Br^- \equiv 1\,\text{mol } BrO_3^- \equiv 3\,\text{mol } I_2 \equiv 6\,\text{mol } S_2O_3^{2-} \quad \text{or} \quad \text{PAO}$$

Or, 1 mol titrant $S_2O_3^{2-}$ or PAO

$$\equiv \frac{1}{6}\,\text{mol } Br^- \equiv \frac{79.9\,\text{g}}{6} \quad \text{or} \quad 13.32\,\text{g} \quad \text{or} \quad 13.320\,\text{mg } Br^-$$

Similarly, for the iodide reaction

$$1\,\text{mol titrant } S_2O_3^{2-} \quad \text{or} \quad \text{PAO}$$
$$\equiv \frac{1}{6}\,\text{mol } I^- \equiv \frac{126.9\,\text{g}}{6} \quad \text{or} \quad 21.15\,\text{g}$$

or 21,150 mg I^-

$$\text{Concentration of } Br^-(mg/L) = (\text{Concentration of bromide} + \text{iodide}) - (\text{Concentration of iodide})$$

$$13{,}220\left(\frac{A \times B}{C}\right) - 21{,}150\left(\frac{D \times E}{F}\right)$$

where

A is the volume of $Na_2S_2O_3$ or PAO in milliliters required to titrate the sample for bromide plus iodide (blank corrected)
B is the normality of $Na_2S_2O_3$ or PAO needed to titrate the sample for bromide plus iodide
C is the sample volume in milliliters used in the titration to determine bromide plus iodide in the sample
D is the volume of $Na_2S_2O_3$ or PAO in milliliters required to titrate the sample for iodide (blank corrected)
E is the normality of the titrant $Na_2S_2O_3$ or PAO used to titrate the sample for iodide
F is the sample volume in milliliters used in the titration for iodide determination

For blank corrections, subtract the milliliters of the titrant used in the blank analysis from the titrant readings *A* and *D*.

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19 Chloride

Chloride (Cl^-) is one of the most commonly occurring anions in the environment. It can be analyzed using several different methods, some of which are listed below:

1. Mercuric nitrate titrimetric method
2. Argentometric titrimetric method
3. Automated ferricyanide colorimetric method
4. Gravimetric determination
5. Ion-selective electrode method
6. Ion chromatography

Methods 1 and 3 are EPA approved (Methods 325.3 and 325.1–2, respectively) for chloride determination in wastewater. For multiple ion determination, ion chromatography technique should be followed (see Chapter 11).

MERCURIC NITRATE TITRIMETRIC METHOD

Chloride reacts with mercuric nitrate to form soluble mercuric chloride. The reaction is shown below for calcium chloride ($CaCl_2$) as a typical example:

$$CaCl_2 + Hg(NO_3)_2 \rightarrow HgCl_2 + Ca(NO_3)_2$$

The analysis may be performed by titrimetry using a suitable indicator. Diphenyl carbazone is a choice indicator that forms a purple complex with excess mercuric ions in the pH range of 2.3–2.8. Therefore, the pH control is essential in this analysis. Xylene cyanol FF is added to diphenyl carbazone to enhance the sharpness of the end point in the titration. Nitric acid is used to acidify the indicator to the required low pH range.

Other halide ions, especially bromide and iodide, are interference in this analysis. Acidify alkaline samples before analysis. Fe^{3+}, CrO_4^{2-}, and SO_3^{2-} at concentrations above 10 mg/L are often used to interfere with the analysis.

Procedure

Add 1 mL acidified indicator reagent to a 100 mL sample. The solution should become greenish-blue. If the color is pure blue, the pH is above 3.8, while a light green color indicates a pH less than 2. The pH adjustment is very crucial in this analysis. Titrate the sample with 0.0141 N $Hg(NO_3)_2$. Prior to the end point, the solution turns blue; at the end point, the color turns purple. Perform a blank titration using distilled water.

$$\text{mg } Cl^-/\text{L} = \frac{(A-B)\times N\times 35{,}450}{\text{Volume of sample (mL)}}$$

where

A is the volume of the titrant, $Hg(NO_3)_2$ required to titrate the sample
B is the volume of the titrant required for the blank titration
N is the normality of $Hg(NO_3)_2$

The number 35,450 is used in the above equation because the equivalent weight of chlorine is 35.45 and, therefore, the milligram equivalent weight is 35,450.

Dilute the sample if it is highly concentrated in chloride (>100 mg/L). Alternately, use a smaller sample portion or $Hg(NO_3)_2$ titrant of greater strength.

Reagents

- Mercuric nitrate titrant (0.0141 N): dissolve 2.288 g $Hg(NO_3)_2$ or 2.425 g $Hg(NO_3)_2 \cdot H_2O$ in distilled water containing 0.25 mL conc. HNO_3. Dilute to 1 L. 1 mL of this titrant + 500 μg Cl^-. (The exact normality of the above-prepared solution may be determined by titrating this solution against NaCl standard using acidified diphenyl carbazone–xylene cyanol FF to the purple end point.) Dissolve 824 mg NaCl (dried at 140°C) in 1 L distilled water to produce 0.0141 N NaCl. 1 mL of this solution + 500 μg Cl^-. Use 100 mL NaCl solution in this titration against $Hg(NO_3)_2$ titrant. Run a blank using distilled water.

$$\text{Normality of } Hg(NO_3)_2 = \frac{1.41}{\text{mL titrant } Hg(NO_3)_2 \text{(blank subtracted)}}$$

- Indicator solution. To 100 mL 95% ethanol or isopropyl alcohol, add 250 mg *s*-diphenyl carbazone, 4 mL conc. HNO_3, and 30 mg xylene cyanol FF. Store in a refrigerator in an amber bottle.

ARGENTOMETRIC TITRIMETRIC METHOD

Silver nitrate reacts with chloride in neutral or slightly alkaline solution, quantitatively precipitating silver chloride as shown below:

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

Potassium chromate also reacts with $AgNO_3$ to form red silver chromate:

$$K_2CrO_4 + 2AgNO_3 \rightarrow Ag_2CrO_4 + 2KNO_3$$

The above reaction, however, is less favorable than the former reaction. Therefore, K_2CrO_4 can indicate the end point of $AgNO_3$ chloride titration. At the end point, when no free chloride is left in the solution, the addition of a drop of $AgNO_3$ titrant results in the formation of Ag_2CrO_4 producing a pink end point.

Several ions interfere in this analysis. These include bromide, iodide, cyanide, sulfide, sulfite, and thiosulfate. The latter three ions may be removed by treatment with H_2O_2. The sample should be diluted when iron and orthophosphate are present at concentrations above 10 mg/L.

Procedure

Adjust the pH of the sample in the range 7–10. To a 100 mL sample, add 1 mL 30% H_2O_2 and stir. Add 1 mL of K_2CrO_4 indicator. Titrate the sample with standard $AgNO_3$ (0.0141 N) titrant to pink end point. Run a blank using distilled water.

$$\text{mg } Cl^-/\text{L} = \frac{(A-B)\times N \times 35{,}450}{\text{Volume of sample (mL)}}$$

where

A is the volume of $AgNO_3$ titrant (mL)
B is the volume of $AgNO_3$ titrant (mL) required for blank titration
N is the normality of the titrant, $AgNO_3$

Reagents

- Standard $AgNO_3$ (0.0141 N): dissolve 2.395 g $AgNO_3$ in 1 L distilled water. This titrant solution is standardized against standard NaCl solution using K_2CrO_4 indicator (see above; by substituting the known concentration for Cl^- in the above equation, the exact normality, *N*, of $AgNO_3$ can be determined. The concentration of chloride, mg Cl^-/L, in the prepared NaCl standard = mg Cl^-/L × 0.6066).
- Potassium chromate indicator solution: dissolve 10 g K_2CrO_4 in approximately 20–30 mL distilled water. Add $AgNO_3$ solution until a red precipitate forms. Allow it to stand for a day. Filter and dilute the volume to 200 mL.

AUTOMATED FERRICYANIDE COLORIMETRIC METHOD

It is a rapid colorimetric determination in which about 15–30 samples may be analyzed per hour using an automated analytical equipment. Chloride at concentration range 1–250 mg/L may be analyzed using this method.

Chloride ion reacts with mercuric thiocyanate forming unionized mercuric chloride, liberating thiocyanate ion (SCN^-). The liberated thiocyanate ion reacts with Fe^{3+} to form a highly colored ferric thiocyanate. These reactions are shown below:

$$2Cl^- + Hg(SCN)_2 \rightarrow HgCl_2 + 2SCN^-$$
$$3SCN^- + Fe^{3+} \rightarrow Fe(SCN)_3$$

The amount of $Fe(SCN)_3$ formed is proportional to the original concentration of the chloride in the sample. Thus, the intensity of the color due to $Fe(SCN)_3$ formed is proportional to the chloride content in the sample.

Procedure

The apparatus used for the analysis is a continuous flow automated analytical instrument such as Technicon Autoanalyzer. Follow the manufacturer's instructions to set up the manifold and for general operation.

Chloride standards are prepared in the concentration range 1–250 mg/L from the stock standard solution (1.6482 g NaCl dried at 140°C dissolved in 1 L distilled water; 1 mL + 1 mg Cl^-). Prepare a standard calibration curve by plotting peak heights against the chloride concentrations of the standards from which the concentrations of Cl^- in the unknown sample is determined.

Reagents

- $Hg(SCN)_2$ solution: 4.17 g in 1 L methanol.
- Ferric nitrate solution: 202 g $Fe(NO_3)_3 \cdot 9H_2O$ in 1 L distilled water containing 21 mL HNO_3. Mix, filter, and store the solution in an amber bottle.
- Color reagent: mix 150 mL $Hg(SCN)_2$ with 150 mL $Fe(NO_3)_3$ solution prepared as above. Dilute to 1 L. Add 0.5 mL Brij 35 (polyoxyethylene 23 lauryl ether).

GRAVIMETRIC DETERMINATION OF CHLORIDE

Gravimetric analysis for chloride in wastewaters does not give accurate results at concentrations below 100 mg/L. This method is rarely applied in routine environmental analysis because it is lengthy and rigorous.

This method is based on the fact that $AgNO_3$ reacts with the chloride anions in the solution, thus precipitating out AgCl. Actually, the latter is produced first as a colloid that then coagulates on heating. HNO_3 and a small excess of $AgNO_3$ favor such coagulation. Avoid adding an excess of $AgNO_3$ because it may coprecipitate with AgCl. Also, avoid exposure of AgCl to sunlight that can cause photodecomposition.

Procedure

To a 100 mL sample acidified with HNO_3 and taken in a beaker, add 0.2 N $AgNO_3$ solution slowly with stirring until AgCl is observed to coagulate. Then, add an additional 5 mL of $AgNO_3$ solution. Heat the sample to boiling for 5 min. Add 1 mL of $AgNO_3$ solution to confirm that precipitation is complete. If the supernatant solution turns white or additional precipitation is observed, keep on adding $AgNO_3$ slowly to the sample mixture until the precipitation is complete. Place the beaker in the dark and allow it to stand overnight or at least for 3 h.

Filter the precipitate using a clean, dry, and accurately weighed sintered glass or porcelain filtering crucible following the decantation of the supernatant liquids first through the filtering crucible. The AgCl should be quantitatively transferred from the beaker to the filtering crucible. Wash the precipitate three to four times with distilled water acidified with a few drops of HNO_3. The washing should be free of Ag^+ ion. If the final washing still contains Ag^+ ion, the precipitate should be subjected to more washings. The presence of Ag^+ in washing may be tested by adding a few drops of HCl to a small volume of washing in a test tube. The solution would turn turbid in the presence of Ag^+ ion.

Calculation

Dry the precipitate at 105°C for 1 h. Place the crucible in a desiccator to cool. Weigh it with its contents. Repeat the steps of heating, cooling, and weighing until two consecutive weights are constant.

$$\text{mg/L } Cl^- = \frac{(B-A)}{V} \times \frac{1\,\text{mol } Cl^-}{1\,\text{mol AgCl}} \times 1000$$

$$= \frac{(B-A)}{V} \times 0.247 \times 1000$$

where

A is the weight of empty dry filtering crucible
B is the weight of the empty dry filtering crucible plus AgCl precipitate
V is the mL of sample

20 Chlorine and Chloramines

GENERAL DISCUSSION

Chlorine is used as bactericide for water treatment. It is added mostly as sodium hypochlorite, NaClO, or sometimes as calcium hypochlorite, $Ca(ClO)_2$, or molecular chlorine, Cl_2 to industrial or municipal wastewater or to pool water. When chlorine is added to water it reacts with water forming hypochlorous acid, HClO.

$$Cl_2 + 2H_2O \rightarrow HClO + H_3O^+ + Cl^-$$

Similarly when a hypochlorite salt is added to water it also forms hypochlorous acid, HClO;

$$NaClO + H_2O \rightarrow HClO + Na^+ + Cl^-$$

Though hypochlorous acid forms in aqueous solution, it is unstable however and cannot be separated out from water. HClO may dissociate back to hypochlorite ion, ClO^-;

$$HClO + 2H_2O \rightarrow ClO^- + H_3O^+$$

In alkaline water however Cl_2 converts into hypochlorite ion as shown below in the net ionic reactions;

$$Cl_2 + 4OH^- \rightarrow 2ClO^- + 2H_2O + 2e^-$$

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

All these three forms of chlorine, namely, hypochlorous acid, HClO, hypochlorite ion, ClO^- and molecular chlorine, Cl_2, all soluble in water, may exist in equilibrium as follows:

$$HClO \rightarrow ClO^- \rightarrow Cl_2$$

Which form of chlorine predominates would depend on the pH and temperature of the water Below pH 2, the predominant form of chlorine is molecular Cl_2. When the pH is raised above 2, the equilibrium favors HClO. At pH 7.4, however, both HOCl and ClO^- are in equilibrium and in equal amounts. At higher pH when the water is alkaline, the equilibrium as shown above shifts to hypochlorite ion, ClO^- which then becomes the predominant form. All three forms are referred usually as chlorine and measured as free chlorine. They are all oxidants and corrode metals such as lead in pipelines.

There are some terms related to chlorine analysis which need to be understood and defined. Water may contain organic materials, metals, or other compounds, such as fertilizer residues that may react with chlorine prior to disinfection. As a result, some amount of chlorine added to water would be lost in such reactions. The amount of chlorine reacting with such substances present in the waters is referred as “chlorine demand.” The remaining chlorine in the water after accounting for its

chlorine demand is referred as "total chlorine." Thus, the term, "total chlorine" is the initial concentration of chlorine added to water less the "chlorine demand" of water. A part of the so-called "total chlorine" may further react with ammonia and organic amines present in the water to form chloramines, such as monochloroamine, NH_2Cl, dichloroamine, $NHCl_2$, and trichloroamine or nitrogen trichloride, NCl_3 and therefore, would not be available for disinfection. This amount of chlorine reacting with ammonia and the organic amines in the water is known as "combined chlorine," while the remaining chlorine available for disinfection is called "free chlorine." For water of high-purity grade, such as the reagent-grade water, the chlorine demand and the combined chlorine should have values close to zero. All these terms defined above and how they relate to each other, are summarized below:

Chlorine demand = Amount of chlorine reacting with organics, metals, and miscellaneous inorganic substances present in the water
Total chlorine = Initial concentration of chlorine added to water—its chlorine demand
Combined chlorine = Amount of chlorine that reacts with ammonia and organic amines present in the water
Free chlorine = Total chlorine—combined chlorine

Residual chlorine (or residual free chlorine) is another term used frequently, which refers to the amount of chlorine that remains in the water after a certain period or contact time. The meanings of these terms in the literature often overlap.

The concentrations of chlorine in the water is monitored to determine if the amount present is adequate to inactivate the bacteria, viruses, and other disease-causing microorganisms for its potable use, and also if the water is protected from any recontamination during its storage. There should not, however, be any undesirable amount of chlorine remaining in the water beyond what is needed, that may mar the taste and the odor of the water or that may react with any trace organics in the water forming carcinogenic organochlorine compounds. For all these reasons, it is essential to measure concentration of chlorine quantitatively.

There are several methods to analyze chlorine in water. They are either the colorimetric or titrimetric analyses. All colorimetric tests are based on comparing the color change caused by the reaction of chlorine with a suitable color-forming reagent added to the sample. The DPD colorimetric test is most widely used. The test is rapid and commonly used to measure free chlorine in the water. Other colorimetric tests include the orthotolidine and syringaldehyde methods. The latter two tests however do not accurately measure chlorine concentrations in water quantitatively as does the DPD colorimetric test. Among the titrimetric methods are the DPD titration, iodometric titration, and the amperometric titration, all of which are highly accurate, though require adequate skill to perform such error-free titrations. Also, chlorine can be measured by the electrode method, however, subjected to error from interference from the presence of Cl^- ion. The chemical reactions and the analytical procedures involving some of these test methods are highlighted below.

COLORIMETRIC METHODS FOR CHLORINE ANALYSIS

DPD Colorimetric Test

N,N-Diethyl-*p*-phenylenediamine, abbreviated as DPD is the color-forming reagent in this test. It is oxidized by chlorine at near-neutral pH to produce a magenta red colored semiquinoid cationic compound, also known as Wurster dye. This specific reaction occurs and manifests the color at low concentrations of chlorine. However, at a higher concentration of chlorine, DPD may be oxidized further to form an unstable imine compound that is colorless. The magenta color of the solution therefore fades due to formation of this imine product. The intensity of the color from the Wuster dye formed is measured by a spectrophotometer or a filter photometer at the wavelength between

510 and 515 nm. The absorbance is proportional to the chlorine concentrations in the water. This reaction is utilized to measure chlorine concentrations at low levels within the range 0.2–4 mg/L and the test is quantitative in this concentration range. The sample should be diluted accordingly if the concentration of chlorine is above this range.

Colorimetric tests kits are commercially available to analyze chlorine in water. Powdered pillows of the color-forming reagents are added to the sample, the solution shaken and the concentration of chlorine is read from the intensity of the color (Hach Company). Such field kits are available to measure chlorine at the sampling sites. The concentrations of chlorine in field water are directly read from a color chart that comes with the field kit.

Syringaldazine Colorimetric Test

This test is also known as FACTS Method, the term FACTS is abbreviated for "Free Available Chlorine Testing with Syringaldazine." The method is based on a color-forming reaction of free chlorine that occurs when treated with 3,5-dimethyl-4-hydroxybenzaldazine or syringaldazine. The reaction is carried out in the pH range of 6.5–6.8. The product is a red purple compound that is relatively stable if the test is performed within the above pH range. A phosphate buffer should be used therefore to control the pH in this range. The absorbance or the transmittance of the product solution is measured at 530 nm to determine chlorine concentration in the water. In this test, like in all colorimetric procedures the concentration is quantified from a calibration standard curve. The concentration of chlorine in the water in this test can be measured in the range 0.1–10 mg/L.

Syringaldazine reagent is prepared by dissolving the solid in 2-propanol by heating and ultrasonic agitation for several hours. The stability of the solution nevertheless is low because of low solubility of both syringaldazine as well as its colored product in 2-propanol. The reagent solution therefore cannot be stored for long. The presence of other oxidizing substances or high concentrations of calcium carbonate in the water, or if the alkalinity of the water is high, can lead to the erroneous results.

Orthotolidine Colorimetric Test

The orthotolidine test is a rapid screening test to measure chlorine in swimming pool water. It is used in the pool-test kit. One to five drops of orthotolidine is added to a few milliliters of water. The solution turns yellow if chlorine is present. The test however is susceptible to error and cannot give an accurate quantitative measurement of chlorine. This is because orthotolidine degrades readily and furthermore yellow is not a strong color for visual observation.

TITRIMETRIC PROCEDURES FOR CHLORINE ANALYSIS

DPD Titration Method

N,N-Diethyl-p-phenylenediamine (DPD) is oxidized by chlorine to a magenta-red colored species. The reaction and the chemical structures of the product formed are shown above under the DPD colorimetric test (Section "DPD Colorimetric Test"). The reaction is fast and occurs ideally under the pH 6.2–6.5. The colored solution is titrated with a standard solution of ferrous ammonium sulfate (FAS) to a sharp colorless endpoint. If free or residual chlorine is to be measured then follow *Procedure 1* below. However, if the total chlorine in water is to be measured, that is, the free and the combined chlorine, then follow *Procedure 2* in which potassium iodide (KI) is added to the mixture of the buffer, DPD color indicator, and the sample before titration with the FAS standard.

Procedure 1 (Free Chlorine). Place 5 mL of phosphate buffer reagent and an equal volume of DPD indicator solution in a titration flask. Alternatively, 500 mg of DPD powder may be added to the buffer instead of the DPD indicator solution. Then, add the 100 mL sample. If the chlorine

concentration is greater than 5 mg/L which may be above the range of the measurement, then the sample should be diluted in distilled water accordingly. The solution is then mixed and titrated immediately with standard solution of FAS to a sharp colorless endpoint. It is important that the DPD indicator must be added to the buffer before adding the sample.

There are no calculations required to determine chlorine concentration. When 100 mL sample is titrated with 0.00282 N FAS standard solution prepared as follows, then the concentration of chlorine, mg Cl as Cl_2/L = mL titrant used. For example, if 100 mL sample requires 2.65 mL of 0.00282 N FAS titrant, the chlorine concentration in the sample would then be 2.65 mg Cl as Cl_2/L.

Procedure 2 (Total Chlorine). This is same as the Procedure 1 above. The only difference is that KI is added to the mixed solution of buffer, indicator, and the sample and titrated with FAS standard. To equal volume of buffer and DPD indicator solution add 100 mL sample, and then add approximately 1 g KI crystals. Mix the solution well and let it stand for 2 min. Then, titrate this mixture with 0.00282 N FAS standard solution to a sharp colorless endpoint. The pink color disappears at the endpoint. The concentration of *total chlorine* in the sample is equal to the milliliter titrant added.

To determine the combined chlorine in the sample, follow the Procedure 1 above that measures the free residual chlorine (the actual chlorine) only. When the pink color decolorizes at the endpoint, add about 1 g KI to this colorless sample mixture and let it stand for 2 min. If there is any combined chlorine (as chloramines) in the sample, then the solution will turn red or pink again after the addition of KI. The mixture is then titrated with the FAS standard solution as before to a colorless endpoint. While the first titration measures the free residual chlorine, the additional amount of titrant required in the second titration should be equivalent to the combined chlorine only. The total amount of the titrant in both the titrations should therefore be equivalent to the total chlorine in the sample.

EXAMPLE 20.1

100 mL freshly collected sample requires 1.2 mL of 0.00282 N FAS titrant for free chlorine and then after adding KI the solution mixture requires an additional 1.7 mL titrant to decolorize at the endpoint then:

Free residual chlorine = 1.2 mg Cl as Cl_2/L
Combined chlorine (as chloramines) = 1.7 mg Cl as Cl_2/L
Total chlorine = (1.2 + 1.7) or 2.9 mg Cl as Cl_2/L

The reagents: They are available commercially or may be prepared as follows:

Phosphate buffer solution—anhydrous disodium hydrogen phosphate (Na_2HPO_4), 24 g, and anhydrous potassium dihydrogen phosphate (KH_2PO_4), 46 g are dissolved in distilled water. This solution is then combined with 100 mL water containing 800 mg disodium ethylenediamine tetraacetate (EDTA) dihydrate. The final volume diluted with distilled water to 1 L. Add 20 mg $HgCl_2$ to prevent any mold growth.

DPD indicator solution—dissolve 1 g DPD oxalate, or 1.5 g DPD sulfate pentahydrate, or 1.1 g anhydrous DPD sulfate in distilled water containing 8 mL 1:3 H_2SO_4 and 200 mg disodium EDTA. The solution is diluted with distilled water to 1 L and stored in a brown glass-stopper bottle in the dark.

Standard FAS titrant—dissolve 1.106 g FAS hexahydrate, $(Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water acidified with 1 mL 1:3 H_2SO_4 and dilute to 1 L with distilled water. The normality of this solution is 0.00282 N and 1 mL is equivalent to 0.1 mg Cl as Cl_2. The titrant prepared above may be stored for 1 month. The strength of the FAS titrant should be checked by standardizing against 0.1 N primary standard solution of potassium dichromate (made by dissolving 4.904 g anhydrous $K_2Cr_2O_7$ in distilled water and diluting to 1 L) as follows:

To 100 mL FAS standard solution prepared above, add 10 mL 1:5 H_2SO_4, 5 mL concentrated H_3PO_4, and 2 mL 0.1% barium diphenylamine sulfonate indicator and titrate with 0.1 N $K_2Cr_2O_7$ primary standard solution to a violet endpoint. The color at the endpoint persists for 30 s.

Standardization of 0.00282 N FAS solution (an alternative procedure to check the normality of the titrant solution made above):

Pipet 10 mL 0.025 N $K_2Cr_2O_7$ (made by dissolving 1.226 g anhydrous $K_2Cr_2O_7$ in 1 L distilled water) into a 250 mL Erlenmeyer flask.

Iodometric Back Titration Method

In the presence of an excess amount of sodium thiosulfate or phenyl arsine oxide (PAO) and using a starch indicator when a standard solution of potassium iodate is titrated with the sample, the color of the solution turns blue at the endpoint. The appearance of blue color at the endpoint signals that all of the sodium thiosulfate, ($Na_2S_2O_3$) or PAO has reacted. The residual chlorine in the sample can be determined by subtracting the amount of standard iodate solution titrated for the sample from the amount of iodate titrated for a blank.

Procedure: Transfer 200 mL sample into a 500 mL Erlenmeyer flask. Into a second flask transfer 200 mL distilled water. Then, add an amount of 5.0 mL of 0.00564 N $Na_2S_2O_3$ or 0.00564 N PAO, measured accurately, into each flask. Stir the solutions. To each of these flasks then add approximately 0.5 g of KI or 1 mL of 5% KI solution followed by 2 mL of 10% phosphoric acid and 1 mL of starch indicator, respectively. Titrate the flask with distilled water while stirring slowly with 0.00564 N KIO_3 from the buret until the solution turns blue after mixing. The first appearance of the blue color that persists after complete mixing indicates the endpoint of the titration. Record the amount of KIO_3 used. This is the blank. Now carry out a titration in the same way for the sample in the other flask and record the value of KIO_3 used. The concentration of residual chlorine is calculated as follows:

mg Cl_2/L = (mL iodate for blank—mL iodate for the sample) × 200/mL sample

For example, if the volume of standard solution of KIO_3 titrant needed to titrate 5 mL of 0.00564 N PAO plus 200 mL distilled water (blank) is 4.8 mL while that needed to titrate 5 mL of 00564 N PAO plus 200 mL sample is 2.7 mL then, the mg Cl_2/L in the sample = (4.8–2.7 mL) × 200/200 mL or 2.1 mg/L

CHLORAMINES

As mentioned above the term combined chlorine is the amount of chlorine added to the water minus the free chlorine (i.e., the residual or left over chlorine), and this refers mostly to the inorganic chloramines, that are monochloroamine, NH_2Cl, dichloroamine, $NHCl_2$, and trichloroamine or nitrogen trichloride, NCl_3 assuming that all chlorine reacts with ammonia, NH_3. However, there may be organic nitrogen compounds in the water that may also react with chlorine to form organic chloramines which may contribute, though to a much smaller extent to the measured chloramines (the inorganic chloramines), based on the assumption that all chlorine reacts with ammonia only.

The inorganic chloramines in the water can be measured by colorimetry, titrimetry, and amperometry methods. One such method, DPD colorimetric analysis is presented in Section "DPD Titration method." At ambient temperature and the pH range 7.5 to 8.0 all the three inorganic chloramines would be produced resulting from the reaction of chlorine with ammonia, and they would be at equilibrium. However, which of these chloramines exists predominantly would depend on the chlorine to nitrogen ratio (Cl_2/N) in the water. It has been calculated that if the ratio is greater than 10.6 the concentration of monochloroamine, NH_2Cl is lower than 2.5 mg/L. That is, higher chlorine contents would relatively favor the formation of di- and trichloroamines.

The specific inorganic amines however can be analyzed by high-performance liquid chromatography (HPLC), and also GC/MS methods. A few methods have been described in the literature. A detailed discussion is beyond the scope of this book. The GC/MS methods follow two different

approaches, one is the head space-GC/MS (HS-GC/MS), the other is the membrane-introduction mass spectrometry (MIMS). The latter uses a six-port injection port and a membrane cell placed in the GC oven. Specific inorganic chloramines are identified from their characteristic mass ions and can be quantified from their abundances measured under SIM mode. The characteristic mass ions (*m/z*) in electron impact ionization mode for the chloramines are as follow (the most abundant ions are listed first):

Monochloroamine, NH_2Cl: 51 ($NH_2{}^{35}Cl$), 52 ($NH_2{}^{37}Cl$)
Dichloroamine, $NHCl_2$: 49 ($N^{35}Cl$), 51 ($N^{37}Cl$), 85 ($NH^{35}Cl_2$), 87 ($NH^{35}Cl^{37}$), and 87 ($NH^{35}Cl^{37}Cl$)
Trichloroamine, NCl_3: 84 ($N^{35}Cl_2$), 86 ($N^{35}Cl^{37}Cl$), 88 ($N^{37}Cl_2$), 119 ($N^{35}Cl_3$), 121 ($N^{35}Cl_2{}^{37}Cl$), and 123 ($N^{35}Cl^{37}Cl_2$) (the farthest ions 119, 121, and 123 are the molecular ions for NCl_3 for the Cl isotopes and confirm its presence)

The detection limits reported are 0.1 mg, 0.02 mg, and 0.06 mg/L for NH_2Cl, $NHCl_2$, and NCl_3, while for free chlorine it is 0.06 mg/L.

Inorganic and organic chloramines may be analyzed by HPLC following derivatization with 2-mercaptobenzothiazole. The reactions produce stable sulfenamide derivatives (–S–N <) that can be analyzed by HPLC using ultraviolet or electrochemical detectors.

21 Cyanate

The formula of cyanate is CNO^-. It is a univalent anion formed by partial oxidation of cyanide (CN^-).

$$CN^- \xrightarrow{O} CNO^-$$

Under neutral or acidic conditions, it may further oxidize to CO_2 and N_2.

The analysis of cyanate is based on its total conversion to an ammonium salt. This is achieved by heating the acidified sample. The reaction is shown below:

$$2KCNO + H_2SO_4 + 4H_2O \rightarrow (NH_4)_2SO_4 + 2KHCO_3$$

The concentration of ammonia (or ammonium) minus nitrogen before and after the acid hydrolysis is measured and the cyanate amount is calculated as equivalent to this difference.

CALCULATION

Thus, the amount of NH_3–N produced from mg CNO^-/L $= A - B$
where

A = mg NH_3–N/L in the sample portion that was acidified and heated
B = mg NH_3–N/L in the original sample portion

Therefore, the concentration of cyanate as mg CNO^-/L $= 3.0 \times (A - B)$.

(In the above calculation for cyanate, the concentration of ammonia–nitrogen was multiplied by 3 because the formula weight of CNO^- is (12 + 14 + 16) or 42, which is three times 14 [the atomic weight of N, as ammonia–N].)

PROCEDURE

Add 0.5–1 mL of 1:1 H_2SO_4 to a 100 mL portion of sample acidifying to pH 2–2.5. Heat it to boiling for 30 min. Cool to room temperature and bring up to the original volume by adding NH_3-free distilled water.

The analysis for NH_3–N after this may be performed by titrimetric, colorimetric, or selective-ion electrode method (see Chapter 23). Analyze for NH_3–N in an equal volume portion of the untreated original sample.

Treat the sample with $Na_2S_2O_3$ to destroy oxidizing substances (such as Cl_2 residual chlorine) that may react with the cyanate. Add EDTA to complex metal ions that may be present in the sample and that may interfere by forming colored complexes with the Nessler reagent.

Preserve the sample with caustic soda to pH > 12 immediately after sampling to stabilize CNO^-.

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22 Cyanide, Total

Cyanides are metal salts or complexes that contain the cyanide ion (CN^-). These cyanides could be subdivided into two categories: (1) simple cyanides such as NaCN, NH_4CN, or $Ca(CN)_2$ containing one metal ion (usually an alkali or alkaline-earth metal or ammonium ion) in its formula unit and (2) complex cyanides such as $K_4Ce(CN)_6$ or $NaAg(CN)_2$ containing two different metals in their formula unit, one usually being an alkali metal and the other a heavy metal. The complex cyanide dissociates to metal and polycyanide ions. The latter may further dissociate to CN^- that forms HCN. The degree and rate of dissociation of complex cyanides depend on several factors, including the nature of the metal, the pH of the solution, and dilution. Cyanide ion and HCN are highly toxic to human beings, animals, and aquatic life.

Cyanide in water may be determined by the following methods:

1. Silver nitrate titrimetric method
2. Colorimetric method
3. Ion-selective electrode method
4. Ion chromatography

SILVER NITRATE TITRIMETRIC METHOD

Cyanide reacts with silver nitrate forming the soluble cyanide complex, $Ag(CN)_2^-$, as shown below:

$$2CN^- + AgNO_3 \rightarrow Ag(CN)_2^- + NO_3^-$$

When all the CN^- ions in the sample are complexed by Ag^+ ions, any further addition of a few drops of titrant, $AgNO_3$, can produce a distinct color with an indicator that can determine the end point of the titration. Thus, in the presence of a silver-sensitive indicator, *p*-dimethylaminobenzal-rhodamine, Ag^+ ions at first combine preferentially with CN^-. When no more free CN^- is left, little excess of the added Ag^+ reacts with the indicator, turning the color of the solution from yellow to salmon. Cyanide concentrations greater than 1 mg/L can be determined by titrimetry.

Alternately, I^- may be used as an indicator. Titrate to first appearance of turbidity (due to the formation of AgI).

Procedure

The alkaline distillate of the sample (see below in colorimetric method, procedure, for sample distillation), containing 1 mL of indicator solution is titrated against the standard $AgNO_3$ titrant from yellow to a salmon color. Perform a blank titration using the same amount of water and caustic soda. Dilute the sample if necessary with dilute caustic soda solution.

$$\text{mg } CN^-/\text{L} = \frac{(A-B)\times 1000}{\text{Volume of original sample (mL)}} \times \frac{\text{Final volume of alkali distillate}}{\text{mL portion of distillate used}}$$

where

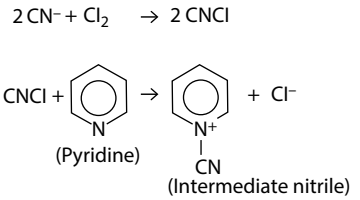
A is the mL of standard $AgNO_3$ solution required to titrate the sample
B is the mL of standard $AgNO_3$ required in the blank titration

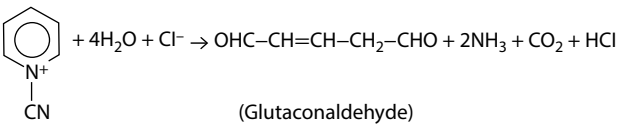
Reagents

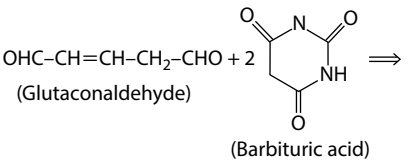
- Standard $AgNO_3$ solution: see Chapter 15 for standardization of $AgNO_3$.
- Indicator solution: 10 mg *p*-dimethylaminobenzalrhodamine in 50 mL acetone.
- Caustic soda dilution solution: 2 g NaOH in 1 L distilled water (0.05 N).

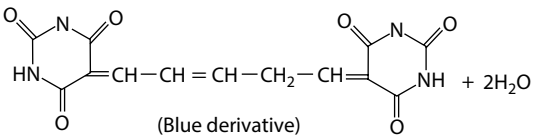
COLORIMETRIC METHOD

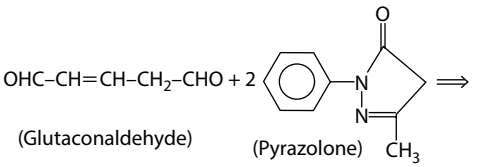
Cyanide is converted to cyanogen chloride, CNCl, by treatment with chloramine-T at pH below 8 without hydrolyzing to cyanate, CNO^-. On addition of pyridine–barbituric acid or pyridine–pyrazolone reagent, the CNCl reacts with pyridine to form an intermediate nitrile that hydrolyzes to glutaconaldehyde. The latter reacts with barbituric acid or pyralozone to give a blue color—the intensity of which is proportional to the concentration of cyanide in the sample. The reaction steps are shown below.

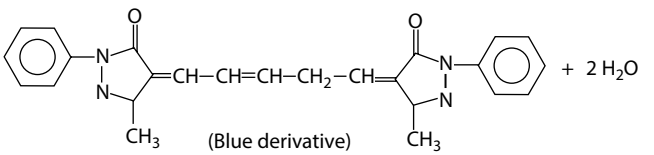












Procedure

Aqueous samples must be distilled to remove interference before analyzing for cyanide. A measured volume of a sample portion is acidified with dilute H_2SO_4 and distilled in a typical cyanide distillation unit. In an acid medium, all cyanides are converted into HCN that is collected over a diluted NaOH solution in a receiving flask. (HCN is absorbed in caustic soda solution.) A portion of distillate is then analyzed for cyanide. HCN is extremely toxic, and therefore, all distillations must be carried out in a hood.

To 80 mL alkali distillate or a portion of the sample in a 100 mL volumetric flask, add 1 mL of acetate buffer and 2 mL of chloramine-T solution and mix by inversion. Some samples may contain compounds in addition to cyanide that may consume chlorine too. Therefore, perform a test for residual chlorine using KI-starch paper, 1 min after adding chloramine-T reagent. (If the test is negative, add 0.5 mL chloramine-T and recheck for residual chlorine 1 min later.) Allow the solution to stand for 2 min. Add 5 mL of pyridine–barbituric acid or pyridine–pyrazolone reagent and mix. Dilute to the mark with distilled water and let it stand for 8 min. Read absorbance against distilled water at 578 nm using a 1-cm cell. Measure absorbance after 40 min at 620 nm when using the pyridine–pyrazolone reagent.

Perform a blank analysis using the same volume of caustic soda dilution solution. Prepare a series of cyanide standards and plot a calibration curve from μg CN^- versus absorbance. The efficiency of the sample distillation step may be checked by distilling two of the standards and then performing the above colorimetric test. Distilled standards must agree within ±10% of undistilled standards.

$$\mu\text{g CN}^-/\text{L} = \frac{A \times 1000 \times V_1}{V_2 \times V_3}$$

where

A is the μg CN^- read from standard curve
V_1 is the final volume of alkali distilled solution (mL)
V_2 is the volume of original sample taken for distillation (mL)
V_3 is the volume of alkali distillate portion taken for colorimetric analysis (mL)

Alternately, the calibration curve may be plotted as ppb concentration of CN^- of working standards versus their corresponding absorbance. In such case, retain the volume of standard solutions same as that of the sample distillate. For example, if the volume of the alkali distillate of the sample is 80 mL before adding reagents, use the same volume of working standard solutions (i.e., 80 mL), for color development and measuring the absorbance for plotting the standard calibration curve. Dilute the sample distillate if the CN^- concentration exceeds the range of the calibration curve.

$$\text{ppb CN}^- = \frac{\text{ppb CN}^- \text{ read from standard curve} \times V_1}{V_2} \times \text{dilution factor (if any)}$$

PREPARATION OF CYANIDE STANDARDS AND CALIBRATION CURVE

Stock cyanide solution: dissolve 2.510 g KCN and 2.0 g KOH (or 1.6 g NaOH) in 1 L water. Standardize this solution against standard $AgNO_3$ solution (see "Silver Nitrate Titrimetric Method" section).

$$1\,\text{mL} = 1\,\text{mg CN}^-$$

Secondary cyanide solution: dilute 1 mL of the above stock solution to 1 L with the caustic soda dilution solution.

$$1\,\text{mL} = 1\,\mu\text{g CN}^-$$

Working CN^- standard solutions: pipette 0, 1, 2, 5, 10, 20, and 40 mL of secondary standard into 100 mL volumetric flasks and dilute first to 90 mL with caustic soda dilution solution and then to a final volume of 100 mL with distilled water after adding buffer and reagents.

Secondary Std. Soln. (mL), 1 mL = 1 μgCN^-	Microgram CN^- in 100 mL of Working Std. Soln.	Microgram CN^- in 80 mL of Working Std. Soln.	Concentration of CN^- in Working Std. Soln. (ppb)
0	0	0	0
1.0	1.0	0.8	10.0
2.0	2.0	1.6	20.0
5.0	5.0	4.0	50.0
10.0	10.0	8.0	100.0
20.0	20.0	16.0	200.0
40.0	40.0	32.0	400.0

Reagents

- Acetate buffer: dissolve 82 g sodium acetate trihydrate in 100 mL water. Acidify to pH 4.5 with glacial acetic acid.
- Chloramine-T solution: 1 g powder in 100 mL distilled water.
- Pyridine–barbituric acid: take 15 g barbituric acid in a 250 mL volumetric flask. Add about 15–20 mL water to wash the side of the flask and to wet barbituric acid. Add 75 mL pyridine and shake to mix. This is followed by addition of 15 mL conc. HCl. Shake well. When the flask is cool, add distilled water diluting to 250 mL. Swirl the flask to dissolve all barbituric acid. Store the solution in an amber bottle in a refrigerator. The solution should be stable for 4–5 months.
- Pyridine–pyrazolone solution: prepared by mixing saturated solutions *a* and *b*. Solution *a* is made by dissolving 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one in 50 mL distilled water by heating at 60°C and stirring. The solution is filtered. Solution *b* is made by dissolving 0.01 g 3,3-dimethyl-1,1-diphenyl-[4,4-*bi*-2-pyrazoline]-5,5-dione in 10 mL pyridine and then filtering. A pink color develops when both the filtrates are added.
- Caustic soda dilution solution: dissolve 1.6 g NaOH in 1 L distilled water.

DETERMINATION OF CYANIDE IN SOIL, SEDIMENT, AND SOLID WASTE

Total cyanide content (which includes water soluble cyanides, iron cyanides, and other insoluble cyanides) in solid matrices may be determined as follows.

To 1 g sample, add 100 mL of 10% caustic soda solution and stir for 12 h. (This treatment is required only if iron cyanides are suspected to be present in the sample.) After this, adjust the pH to less than 8.0 with 1:1 H_2SO_4. Add about 0.2 g sulfamic acid to avoid nitrate/nitrite interference. This is followed by addition of 25 mg lead carbonate (to prevent interference from sulfur compounds). The mixture is distilled and collected over the NaOH solution. This distillate is analyzed for CN^- by colorimetric, titrimetric, or ion-selective electrode method.

$$\text{CN}^- \text{ in the solid matrix, mg/kg} = \frac{\text{mg/L CN}^- \text{ in the leachate} \times \text{volume of leachate (L)} \times 1000}{\text{Weight of sample (g)}}$$

CYANIDES IN AEROSOL AND GAS

Hydrogen cyanide and cyanide salts in aerosol and gas may be analyzed by the NIOSH Method 7904 (Appendix G).

Between 10 and 180 L of air at a flow rate of 0.5–1 L/min is passed through a filter–bubbler assembly of a 0.8 μm cellulose ester membrane and 10 mL of 0.1 N KOH solution. While cyanide particulates retain over the filter membrane, HCN is trapped over the KOH solution in the bubbler. The membrane filter is then placed in 25 mL of 0.1 N KOH solution for 30 min to extract the cyanide particulates deposited on it. The KOH extract and the bubbler KOH solution are analyzed for cyanide by selective-ion electrode technique (see Chapter 9 for a detailed analytical procedure) using KCN standards. Calculate the concentration of particulate CN^- in the sampled air as follows:

$$\text{Particulate CN}^- = \frac{M_\text{f} - B_\text{f}}{V} \text{mg/m}^3$$

where

M_f is the mass of CN^- present in the sample filter (μg)
B_f is the mass of CN^- in the average media blank filter (μg)
V is the volume of sampled air (L)

Similarly, the concentration of HCN in the sampled air is determined as follows:

$$\text{mg HCN/m}^3 \text{ air} = \frac{(M_\text{b} - B_\text{b}) \times 1.04}{V} \text{mg/m}^3$$

where

M_b is the mass of CN^- in the bubbler (μg)
B_b is the mass of CN^- in the blank bubbler
V is the volume of sampled air (L)

The stoichiometric conversion factor from CN^- to HCN is the ratio of the formula weight of HCN to that of CN^-, which is 27/26 or 1.04.

To express mg/m^3 HCN in ppm concentration at 25°C and 1 atm pressure, calculate as follows:

$$\text{ppm HCN} = \frac{\text{mg/m}^3 \text{ HCN}}{1.1}.$$

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23 Cyanide Amenable to Chlorination

This test is performed to determine the amount of cyanide in the sample that would react with chlorine. Not all cyanides in a sample are amenable to chlorination. While HCN, alkali metal cyanides, and CN^- of some complex cyanides react with chlorine, cyanide in certain complexes that are tightly bound to the metal ions are not decomposed by chlorine. Calcium hypochlorite, sodium hypochlorite, and chloramine are some of the common chlorinating agents that may be used as a source of chlorine. The chlorination reaction is performed at a pH between 11 and 12. Under such an alkaline condition, the cyanide reacts with chlorine to form cyanogen chloride, a gas at room temperature that escapes out. Cyanide amenable to chlorination is therefore calculated as the total cyanide content initially in the sample minus the total cyanide left in the sample after chlorine treatment.

Cyanide amenable to chlorination = Total CN^- before chlorination – Total CN^- left after chlorination.

PROCEDURE

Two 500 mL aliquots, or the volume diluted to 500 mL are needed for this analysis. Perform the test for total CN^- in one aliquot of the sample following distillation.

To the other aliquot, add calcium hypochlorite solution (5 g/100 mL) dropwise while maintaining the pH between 11 and 12 with caustic soda solution. Perform a test for residual chlorine using KI-starch paper. The presence of excess chlorine is indicated when the iodide–starch paper turns to a distinct blue color when a drop of the solution is poured on the paper. If required, add additional hypochlorite solution.

Agitate the solution for 1 h. After this period, remove any unreacted chlorine by adding one of the following: (a) 1 g of ascorbic acid, (b) a few drops of 2% sodium arsenite solution, or (c) 10 drops of 3% H_2O_2, followed by 5 drops of 50% sodium thiosulfate solution. Ensure that there is no residual chlorine as indicated from no color change in the KI-starch paper.

Distill this chlorine-treated sample aliquot for cyanide analysis using colorimetric, titrimetric, or ion-selective electrode method outlined in the preceding sections.

ALTERNATIVE PROCEDURE

This is an easy and short method that does not require the distillation of the sample. It is applicable when the CN^- concentration is less than 0.3 mg/L. For higher concentration, dilute the sample. This method determines the HCN and cyanide complexes that are amenable to chlorination. Thiocyanate is positive interference in this test. High concentration of total dissolved solids (>3000 mg/L) may affect the test result. To compensate for this, add an equivalent amount of NaCl in NaOH solution.

Adjust the pH of the sample to between 11.5 and 12. To 20 mL of sample in a 50 mL volumetric flask, add 5 mL of phosphate buffer and two drops of EDTA solution. Add 2 mL chloramine-T solution and stir well. Test for residual chlorine using KI-starch paper. If required, add more chloramine-T so that there is enough residual chlorine in the solution. Allow the solution to stand for exactly 3 min. After this, add 5 mL pyridine–barbituric acid and mix well. Dilute to 50 mL mark. Let the solution stand for 8 min. Measure the absorbance at 578 nm in a 1 cm cell against distilled water. Determine the CN^- concentration from the calibration curve.

$$\text{Cyanide amenable to chlorination, mg/L (ppb)} = \frac{\text{ppb } CN^- \text{ read from calibration curve} \times 50}{20\,\text{mL}}$$

The above procedure is similar to the analysis of total cyanide in the alkaline distillate described in the preceding section, except that the sample's pH is different. In the above method, chlorination is done on the alkaline sample at a pH between 11.5 and 12. On the other hand, in the determination of cyanide (total), the pH of the distillate is maintained below 8 with the acetate buffer before adding chloramine-T solution.

Thiocyanate interferes in the above test. If thiocyanate is found to be present in the sample (see thiocyanate, spot test), cyanide is masked by adding formaldehyde solution. The sample is then analyzed to determine the amount of thiocyanate that would react with chlorine. Thus, the cyanide amenable to chlorination is equal to the difference between CN^- concentrations obtained in the untreated and formaldehyde-treated sample aliquots.

To a 20 mL aliquot of sample adjusted for pH between 11.5 and 12, add two to three drops of 10% formaldehyde solution. Stir and then allow the solution to stand for 10 min. After this, add the reagents and follow the procedure given above to determine the cyanide amenable to chlorination by the colorimetric method.

REAGENTS

See also preceding section.

- Calcium hypochlorite solution (5%): 5 g in 100 mL distilled water; store in dark in an amber glass bottle.
- EDTA solution 0.05 M: 1.85 g ethylenediaminetetraacetic acid disodium salt in water to 100 mL.
- Phosphate buffer: 13.8 g sodium dihydrogen monohydrate, $NaH_2PO_4 \cdot H_2O$ dissolved in water to 100 mL.
- Formaldehyde solution (10%): dilute 27 mL of 37% commercial grade solution to 100 mL with water.

24 Emerging Pollutants
Classification, Extractions, and Analytical Techniques—An Overview

GENERAL DEFINITION AND CLASSIFICATIONS

The term, "Emerging Pollutants" include a wide range of substances of various categories, and their classifications are based on their usage, applications, and chemical properties. They are released into the environment, originating from industrial wastes, or produced as by-products from agrochemicals, pesticides, pharmaceuticals, household chemicals, and other substances of human use—or their degradation residues. The broad definition of emerging pollutants also include many naturally occurring substances, along with the synthetic chemicals that are not commonly monitored in the environment, that however have the potential to enter into the environment and cause adverse effects on human health and ecology. They are released into the environment directly or indirectly by various routes and exposures to such substances and may produce adverse impacts on humans, animals, aquatic species, and vegetations. These substances, numbering close to 1000, have been detected in the environment but do not have regulatory standards and are therefore not currently included in routine monitoring programs. The risk and fate assessment studies related to several such emerging pollutants, especially the toxic ones, are currently under study. Some general types of pollutants based on their broad applications are listed below in Table 24.1.

It may be noted that several compounds of similar applications and often similar types of chemical structures are regulated though and listed as "priority pollutants." However, there are also several additional substances in these categories that have been detected in the environment for which there are currently no monitoring criteria yet. As for example, while di-n-butyl phthalate, a plasticizer and a low-acute toxic endocrine disrupter often found to occur in many environmental waters is regulated, there is, however no such criteria for two other similar phthalate esters, namely, diisononylphthalate and diisodecylphthalate. The latter two substances should therefore be termed as emerging pollutants. Also while there are many substances belonging to specific classes of emerging pollutants, such as, all the chlorophenoxy acids herbicides, or all barbitals that may fall under the same structural features, there are, also substances categorized under the headings, such as, pharmaceuticals or human personal care products that may vary widely in their chemical structures. Some typical examples of such pollutants having same types of chemical structures, containing the same functional groups are discussed below.

The toxic properties of many such emerging pollutants may also vary widely. Some are highly toxic, while many exhibit much lower acute effects. For example, while substances belonging to the class of organic phosphates used for pest control in crops, such as, bromofos ethyl, and likewise many carbamates that are inhibitors of acetylcholinesterase, may manifest a high degree of acute toxicity, many industrial and laboratory chemicals, such as hydrazine or chloral hydrate however exhibit relatively a much lower degree of toxicity by all routes.

SAMPLE EXTRACTIONS

The extraction steps for most of these emerging pollutants of the types listed in Table 24.1 should not be any different from that used in general environmental analysis. For aqueous samples, the

TABLE 24.1
Classifications of Emerging Pollutants of General types

Types	Examples
Human personal care products	Fragrances, essential oils, antibacterials
Human medicines	Ibuprofen, sulfonamide, statins, tetracycline
Veterinary medicines	Antibiotics and antiparasitic agents
Hormones	Estrogens and androgens
Agrochemicals	Pesticides, herbicides, fertilizer residues
Pesticides	Phosphate esters, carbamates, chlorophenoxy acids
Flame Retardants	
Detergents/cleaning agents	Surfactants, dry cleaning solvents
Nanomaterials	Carbon nanotubes, nanogold
Plasticizers	Phthalate esters of long chain
Disinfection by-products	Halogen substituted acids and derivatives
Naturally produced toxins	Produced by fungi, bacteria, and plants
Substances of abuse	Cannabis, cocaine, ecstasy
Particulate matters	Mining, ore processing, and industrial processes
Miscellaneous chemicals	Industrial and laboratory chemicals

two most common techniques are the LLE and the solid phase extraction (SPE). The LLE involves using a water-immiscible solvent for extraction in which the pollutants must have greater solubility in that solvent than in water, and therefore partition into the solvent from the aqueous phase. Repeated extractions give better separation than a single extraction. Methylene chloride (dichloromethane) which is used for many U.S. EPA methods should be also a suitable solvent for such extraction. Other halogenated solvents, such as chloroform (trichloromethane) may alternatively be used. If the water-immiscible solvent is heavier than water, the extraction can be carried out in separatory funnels. However, if the extracting solvent is lighter than water and the pollutants are also hydrophobic in nature, then the extractions may be carried out effectively using a smaller volume of samples in vials with a few milliliters of a hydrophobic solvent, such as hexane, isooctane, or toluene (microextraction). The separatory funnel LLE, however, requires use of larger volume of samples and also extraction solvents. Also sample concentration steps may be needed to achieve the desired detection levels and the overall procedures therefore can be time consuming. The microextraction on the other hand is faster and uses much less solvent. The methylene chloride—separatory funnel extractions always form emulsions between the aqueous and the solvent phases due to very slight solubility of methylene chloride in water and therefore, such procedures would require breaking of emulsions by various means. The extraction procedures using hydrocarbon solvents, although does not form emulsions at the solvent–water interface, and therefore, a few microliters solutions from the upper solvent phase can be conveniently injected into the GC, the method however might not be able to give low detection levels in accordance to the regulatory requirements. An additional concentration step for the solvent extracts may then be needed. Also, continuous LLE procedures may be carried out in lieu of the manual steps, however such extraction may require 12–24 h.

LLE procedures may be applied for extracting all classes of emerging pollutants including flame retardants, plasticizers, disinfectants, pharmaceuticals, alkylphenol ethoxylate nonionic surfactants, and disinfectants.

SPE offers many advantages over LLE in terms of cost and speed. Also, many hydrophilic pollutants do not partition effectively into an organic solvent for which the extraction efficiency of LLE may be poor. SPE can be carried out *in situ* at the sampling site to avoid the need for transportation to the laboratory or storage of large volume of water samples if using a portable GC for

field analysis. These are some other advantages of SPE. At present, SPE methods are cited mostly in the literature in regard to extraction of emerging pollutants. A few general methods are briefly discussed below. The selection of an extraction method however should be based on several factors, including the detection level desired, availability of materials, convenience, cost, and time, and should therefore be one's personal choice.

SPE may be carried out in one of three formats, using (1) small cylindrical cartridges, (2) thin flat discs, or (3) well plates. These devices are available commercially. When SPE cartridges are used, about 5–6 mL of aqueous sample is loaded on the cartridge. The flat discs are usually either 47 mm or 90 mm in size. A very large volume of sample, for example, 5 L can be extracted on 90 mm styrene–divinylbenzene SPE discs. The sorbents used for SPE are generally of a wide variety, based on their ability to retain the pollutants, which primarily depends on the polarity of the pollutants, and also on other factors. The sorbents used may be classified broadly into four types: (i) octadecyl (C_{18})-, or octyl (C_8)- carbon chain or similar group bonded to silica; (ii) polyvinylstyrenes; (iii) hydrophilic–lipophilic balanced (HLB) adsorbents; and (iv) the ion exchange resin-type sorbents, that include both the strong or weak cation or anion exchange resins. Such ion exchange resins can also be used for sample concentration or for cleanup.

The octadecyl (C_{18})—SPE separations can be carried out for many neutral pharmaceuticals, such as diazepam, phenylbutazone, and caffeine. In such extraction, a sample volume of 500 mL–1 L is first pH adjusted to 7–7.5 and then loaded on the sorbent disc. The adsorbed pharmaceuticals are then eluted subsequently with a small volume of methanol (1–3 mL). The extract is further concentrated down to 20–25 uL and then diluted with phosphate buffer to a final volume of 1 mL for analysis.

A sorbent mixture of polystyrene and poly(methylmethacrylate) packed between polyethylene frits is used in the extraction of natural and synthetic musk, such as tonalide, versalide, and cashmeran. A large volume of sample, about 50 L can be extracted effectively.

Hydrophilic–lipophilic mix type sorbents can be used for extracting hormones, such as, estrogens, progestrogens, and their synthetic counterparts, such as, diethylstilbestrol and ethynylestradiol from aqueous matrices. Such sorbent cartridges can be utilized for simultaneously extracting neutral and acidic pharmaceuticals and certain pesticides from waters. One liter of aqueous sample, pH adjusted to 3, may be loaded on such sorbent mix and the adsorbed pollutants may be eluted with a small volume of ethyl acetate–acetone solvent mixture. The solvent extract may then be analyzed by GC/MS for the neutral compounds while the acidic pharmaceuticals can be esterified with diazomethane and their methyl esters can be determined in a second GC/MS run. It may be noted here that such pollutants may also be extracted using other sorbents, such as, octadecyl-bonded silica, and polydivinyl-styrene resins. The presence of certain interfering substances in the sample may however mar the extraction efficiency of the SPE sorbents. Both HLB sorbents and octadecyl bound silica find applications in extractions of both basic and acidic pharmaceutical compounds. Examples of such substances include aspirin, caffeine, carbamazepine, and naproxen. A typical procedure of such extraction is highlighted below.

One liter aqueous sample is first filtered to remove any solid or floating particles. It is then acidified to pH below 2 and extracted using a HLB cartridge/disc at a rate of 15 mL/min. The cartridge is dried under nitrogen flow for 1 h. The pollutants are eluted first with 2 mL ethyl acetate, and then ethyl acetate/acetone (1:1 mixture) and finally with 2 mL of ethyl acetate/acetone mixture containing one to two drops of ammonium hydroxide. The extracts are evaporated and the residues dissolved with 200 uL ethyl acetate and treated with N-methyltrimethylsilyltrifluoroacetamide (MSTFA) (Chapter 14) to derivatize the acidic compounds, such as, aspirin, ibuprofen, diclofenac, and naproxen. The pollutants (that are the basics) and/or their derivatives (the acidic pharmaceuticals) are analyzed by GC/MS. A number of pharmaceuticals including corticosteroids, such as cortisone and prednisone and the beta-blockers such as atenolol, metoprolol, and propanolol can alternatively be extracted by SPE cartridges packed with mixed cation exchange sorbents. Highlighted below is one such typical procedure.

A 500 mL sample aliquote, acidified with formic acid is loaded onto the mixed cation exchange sorbent. While the corticosteroids are eluted with 1 mL methanol/water mixture (70:30) to which a few drops of formic acid added, in the second stage elution, the beta-blockers are desorbed with methanol/ammonia solution (95:5). The eluants are evaporated to dryness and then dissolved in a mixture of acetonitrile/water (25:75) and the analytes are analyzed by LC–MS/MS.

Many alkylphenolic compounds including phenylphenol and bisphenol A in waters at neutral pH can be extracted by SPE on HLB sorbent cartridges. The cartridges are dried and the analytes eluted with 1:1 mixture of methyl-*tert*-butyl ether/2-propanol followed by methanol. The eluant evaporated to a very small volume and then diluted with 1:1 methanol/water to a final volume of 0.5 mL for analysis by LC–MS/MS.

Many perfluorinated compounds that are used as surfactants and surface protective chemicals are found ubiquitously in the environment because of their wide applications. Such compounds include perfluorooctanesulfonate and perfluorooctanoate. Aqueous samples are acidified to pH below 3 and extracted by SPE on octadecyl (C18)- sorbent cartridges and analyzed by LC/MS or LC–MS/MS.

Microextraction techniques have also been reported in the literature for extractions of many types of emerging pollutants. Such methods include both the liquid–liquid microextractions (LLME) and the solid phase microextractions (SPME) involving small volumes of samples in microliter amounts. The LLME methods use disposable polypropylene hollow fibers and the extract phase does not come into contact with the sample. The SPME techniques use hollow fibers of both types: the liquid coatings and the solid coatings. In the liquid coating hollow fibers, the pollutants are absorbed into the liquid coatings whereas in case of the solidcoating SPME, the pollutants adsorb onto the solid surface of the coating materials. Polymers implanted with large number of hydroxyl (–OH) functional group are described for SPME in the literature for extraction of polar compounds, such as steroids and hormones. In SPME, as in LLME the sample volume needed is small. The volume of solvent is also small. However, presence of interfering substances in the samples, such as humic acid or surfactants, that may compete for the bonding sites on the surface may mar the efficiency of extractions.

ANALYSIS

The solvent extracts from LLE, SPE, LLME, or SPME are analyzed by GC or LC interfaced to a suitable detector. The compounds are separated on appropriate GC or HPLC columns and detected by a GC or HPLC detector. Most studies on their analyses, however describe the use of mass spectrometry. Traditional GC or LC detectors may be used in lieu of a mass selective detector to screen and quantify a target compound or a list of target compounds. For example, HPLC—fluorescence detection has been described for estrogens in environmental samples. It may sometimes be difficult to identify the target compounds, especially in presence of interferences. Cleanup of sample extracts, running the analysis on an alternate column, spiking standard solutions of analytes to the extracts, or other general techniques may, therefore become essential for screening the target pollutants.

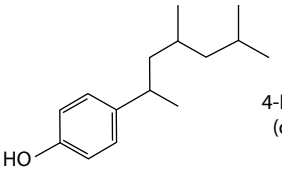
All recent work cited in the literature pertaining to the analysis of various classes of emerging pollutants describe the mass spectrometric techniques (GC/MS and LC/MS). The selection of an analytical method however should depend on achieving the desired detection levels and also on regulatory requirements. A variety of mass spectrometers are now used, that include the quadrupole, ion trap, magnetic sector, triple quadrupole, and time-of-flight mass analyzers. The mass spectrometric determination of a compound may be carried out either under the scan or the selective ion monitoring (SIM) mode. The SIM mode should be preferred for quantification of a substance. The characteristic mass ions for the compounds to confirm their presence and quantification may be found in the literature. The GC, GC/MS, and HPLC techniques are described in Chapters 3, 4, and 10, respectively. Analytical procedures for different classes of emerging pollutants are presented in Chapters 25 through 29.

25 Emerging Pollutants
Nonionic Surfactants—Alkylphenols and Their Ethoxylates

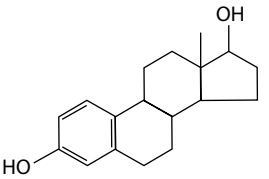
The nonionic surfactants, alkylphenol ethoxylates, have the highest production rates among the surfactants used in industrial and domestic applications. Although the domestic applications of these compounds have declined significantly in recent years, their use in industrial detergents and other industrial processes such as wool washings have continued unabatedly. Phenol ethoxylates are also used in paints, agrochemicals, emulsion polymers, textiles, and metal finishing and, sometimes, as antioxidants in plasticizers. Alkylphenol ethoxylate surfactants are usually made from the branched-chain alkylphenols, mostly nonylphenol (NP) and octylphenol by reactions with ethylene oxide. Over 75% of alkylphenol ethoxylates used in industries constitute NP ethoxylates, the remaining are the octylphenol ethoxylates. In commercial formulations that are usually complex mixtures of homologues, oligomers, and isomers, the length of the ethoxylate chain varies between 1 and 50 ethoxy units, depending on the use. These substances biodegrade in the environment producing alkylphenol monoethoxylates and diethoxylates, alkylphenol acetic acids, alkylphenolpolyethoxyacetic acids, and alkylphenols (Warhurst, 1995). Such degradation products resulting from the loss of ethoxy groups are relatively more stable and less biodegrading in the environment than are the alkylphenol ethoxylates. The longer chain alkylphenol ethoxylates usually degrade into their alkylphenols while the shorter chain surfactants of this class break down to mono-, di-, and triethoxylate derivatives under ambient environmental conditions. These surfactants and their degradation products are commonly found in many wastewater discharges and effluents of sewage treatment plants. These substances have received significant attention because of their ubiquitous presence in wastewater and, more importantly, because they are thought to be the precursors of estrogenic metabolic products generated during wastewater treatment. There is a great concern that the metabolites of these surfactants, namely, the nonyl- and octylphenols and their mono-, di-, and triethoxylates can mimic natural hormones. In addition, the levels at which they persist in the environment is sufficiently high to disrupt the endocrine function in fish, wildlife, and humans (Ying et al., 2002). These metabolites accumulate in organisms. The bioconcentration factors may vary from 10 to several thousand depending on the nature of the metabolite, species, and the organ. Several phenolic xenoestrogens as well as many other types of endocrine-disrupting chemicals have been found in the air, river, and canal waters, and sediment samples in the United States, Europe, and several other countries (Brossa et al., 2005; Heemken et al., 2001; Jackson and Sutton, 2008; Petrovic et al., 2002).

STRUCTURES

The chemical structure of one of the isomers, the *para*-isomer of NP (4-*n*-NP) is shown below against that of oestradiol. The similarity in both their structures reflect the fact that NP, the major metabolite of alkylphenol ethoxylates, is xenoestrogenic. Other metabolites of these nonionic surfactants too mimic natural hormones.

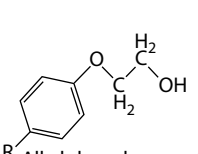


4-Nonylphenol
(one isomer)

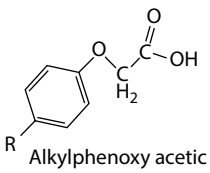


17β-Oestradiol

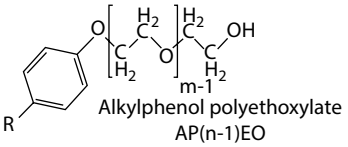
NP ethoxylates have the general structure (NP*n*EOs) where *n* is the number of ethoxy units ($–CH_2CH_2O–$) that are attached to the phenol ring of NP via the phenolic –OH group. Similarly, the general structure for alkylphenol ethoxylates is Ap*n*EOs, where AP is alkylphenol, usually the nonyl-, or octylphenol. The chemical structures of the alkylphenol monoethoxylate, AP1EO and the corresponding acetic acid derivative, alkylphenoxy acetic acid, AP1EC, and their polyethoxy analogs, alkylphenol polyethoxylate, Ap*n*EO and alkylphenol polyethoxycarboxylic acids, AP*n*EC are shown below. The commercial products contain mixtures of several isomers in which the nonyl and the octyl groups are attached onto the phenol ring mostly at the *para*-position and in a few isomers at the *ortho*-position. These alkyl groups are usually branched chains. In addition, the number of ethoxy groups in such alkylphenolethoxylate isomers in these surfactants may vary. As mentioned above, the metabolites of these surfactants resulting from their biodegradation and found in environmental matrices are largely the nonyl- and octylphenol, their mono-, and diethoxylates and their phenoxy acetic acid or the phenoxycarboxylic acid derivatives. The methods of analysis of these metabolites are briefly discussed below.



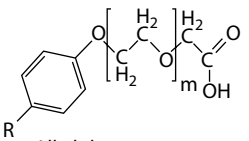
Alkylphenol monoethoxylate
(APIEO)



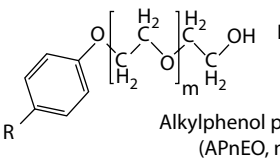
Alkylphenoxy acetic acid
(APIEC)



Alkylphenol polyethoxylate
AP(n-1)EO



Alkylphenoxy
carboxylic acid (APnEC)



$R = C_8H_{19}$ nonyl
C_8H_{17} octyl
R is usually branched

Alkylphenol polyethoxylate
(APnEO, n = m + 1)

SAMPLE EXTRACTIONS AND ANALYSIS: GENERAL DISCUSSION

These substances may be determined by LC/MS or GC/MS following their extractions from water, soil, and sediments. In addition, these compounds can be analyzed by HPLC-fluorescence,

HPLC-UV, and GC-FID. Since such surfactants used commercially are mixtures of several oligomers and isomers, LC/MS is the preferred method of analyses. Several procedures are described in the literature. Most of these methods are based on LC/MS, while a few describe GC/MS or LC—fluorescence detection. Some of these analytical procedures are briefly outlined below. The LC/MS and GC/MS procedures are briefly discussed below. The LC/MS analysis involves reversed phase LC separation of the compounds followed by their mass spectrometric detection using either atmospheric chemical ionization or ESI. SPE procedures for isolation of compounds from aqueous samples are generally discussed in most works. Pressurized liquid extraction may be applied for solid samples. Ultrasonic solvent extractions or sonication methods are also equally suitable for soil, sediments, and other solid samples. Soxhlet and microwave-assisted extraction techniques may be applied too. Such extractions are usually followed by SPE cleanup steps before analysis.

Petrovic and coworkers (2002) have described one such general analytical procedure based on SPE followed by LC/MS analysis. The solvent extracts in their method are analyzed by LC/MS under both atmospheric pressure chemical ionization and the EIS. Alkylphenols, alkylphenol ethoxylates, alcohol ethoxylates, and linear alkylbenzene sulfonates were measured in sediment and water samples by this procedure. Many halogenated derivatives of alkylphenol ethoxylates can also be measured by similar methods (Petrovic et al., 2001). The detection limits for these substances in water samples have been reported to range between 20 and 100 μg/L and that for sediment samples from 2 to 10 μg/kg. For sample extraction, C-18 SPE cartridges are most common for extracting aqueous samples. Other types of cartridges, such as Oasis HLB, EnviChrom P, and Isolute ENV+ are also suitable for use. The recoveries and extraction efficiency of target compounds on these cartridges do not seem to vary with the sample pH range from 4 to 8. An LC/MS procedure using an electrospray interface reports lower detection limits in the range 0.06–17.5 μg/L for NP and its ethoxylates (Cespedes et al., 2006).

Brossa and coworkers (2005) have described the analysis of these substances and other endocrine disrupting compounds in environmental waters using two different approaches in their separation and analyses. The authors have compared both these methods. While one procedure involves the SPE online coupled to a GC/MS system through an online interface, the other method uses offline SPE for sample extraction followed by HPLC–electrospray MS analysis in the negative ionization mode. Both these methods are suitable for water analysis and can achieve detection of alkylphenols and their ethoxylates at the levels of low μg/L. In addition, these methods can be applied to measure other endocrine disrupting compounds, especially, the phthalates and adipates types. Andreu and coworkers (2007) have described a method to measure these nonionic surfactants and their metabolites in soil at concentrations ranging from 1 to 100 μg/kg. Their procedure involves isolation of the analytes from the soil samples under pressurized liquid extraction using acetone–hexane mixture (50:50 v/v). The sample extracts are then cleaned up by SPE on a C-18 adsorbent column. The compounds are then analyzed by LC/MS under atmospheric chemical ionization mode. While the alkylphenol polyethoxylates and alcohol ethoxylates were identified as their corresponding ammonium adducts, $[M + NH_3]^+$, the nonyl- and octylphenols were monitored as their deprotonated molecules, $[M - H]^-$. The percent spike recoveries for these substances in this study ranged from 89% to 96%.

Although the extraction and analytical procedures discussed above seem to have many similar features, there could be some significant or even major variation in specific steps. Alternative analytical methods may be followed if they suit the purpose. Although the LC/MS is the most suitable technique of measuring these substances in the environmental matrices, GC/MS may alternatively be used if the compounds to be determined involve isomers with lower molecular masses containing a few ethoxy groups ($–O–CH_2–CH_2–$) in the chain and that are not the oligomers with larger molecular masses. The characteristic mass ions for NP [25154-52-3] by GC/MS under electron impact ionization are *m/z* 149 (primary mass ion), 107, 121, 55, and 77 (secondary ions) and 220 (molecular mass ion). It may be noted here that the technical-grade NP is a mixture of several isomers, the separation of which may always become problematic. One approach to achieve their separation involves fractionation of these isomers, most of which are branched on a capillary GC

column. The instrument for this should have cold injection systems, fraction collectors, and several traps. Meinert and coworkers (2007) have described one such procedure to separate the isomeric mixtures of NP on a capillary GC column and analyzing the compounds isolated simultaneously with a FID and a mass spectrometer. The separated isomers are identified from their RTs, as well as, mass spectra. Gatidou and coworkers (2007) have described a GC/MS method to identify and quantify NP, NP monoethoxylate, NP diethoxylate, bisphenol A, and triclosan in wastewater and sewage sludge. The analytical procedure described by these authors involves derivatization of the target analytes with the compound, bis(trimethylsilyl)trifluoroacetamide or with bis(trimethylsilyl) acetamide. The former, however, is a better derivatizing agent than the latter, as the derivatization reactions with the former proceed faster, producing narrower and higher chromatographic peaks having more precise RTs than the derivatives obtained with the latter. The compounds prior to their derivatization are extracted from the aqueous matrices by SPE techniques and from the solid and sludge samples by sonication. Solid samples may also be extracted by other techniques, including Soxhlet extraction, pressurized liquid extraction, and microwave-assisted methods. The efficiency of SPE depends on the nature of the sorbent material and the organic solvent used for the elution. The recoveries of compounds from the solid matrices by sonication, furthermore, depend on the sonication time and the temperature. Two analytical procedures, one based on LC/MS and the other on GC/MS are outlined below. Sample extraction steps are also highlighted in these procedures.

SPE–LC/MS Method (LC Tandem MS [LC-MS/MS])

Loos and coworkers (2007) have described the following procedure to determine octyl- and NP and their ethoxylates and carboxylates in wastewater-treatment plant effluent and surface waters. The aqueous samples are extracted by SPE on Oasis HLB columns (200 mg/6 mL). The SPE cartridges are first activated and conditioned with 5 mL methanol and 5 mL water, respectively, at a flow rate of 5 mL/min. After this, a volume of 400 mL sample is passed through the wet cartridge at a flow rate of 5 mL/min. The column is then rinsed with 2 mL water at a flow rate of 3 mL/min. The cartridge is then dried under nitrogen at 0.6 atm pressure for 30 min. The analytes are eluted from the cartridge using 3 mL aliquot twice with a solvent mixture of methanol/acetone/ethyl acetate (2:2:1) containing 0.1% formic acid. The sample extract is then concentrated down to a final volume of 0.5 mL under a gentle stream of nitrogen at 40°C in a water bath.

The compounds in the sample extract are separated on an LC column by reversed-phase LC and determined by ESI/MS using atmospheric-pressure ionization. A triple-quadrupole MS/MS system is used in the negative or positive ionization modes in the analysis. The LC and MS conditions in this method are as follows:

LC Column: Synergi Polar-RP (Phenomenex, Torrance, California), 150 × 2 mm, 4 um particles or Superspher 100 RP-18 (Merck, Darmstadt, Germany), 250 × 2 mm, 4 um particle, the former column produces sharper peaks and requires lower flow rate; eluant: water/acetonitrile (water phase is to be acidified with 0.1% acetic acid to pH 3.5 for multicomponent separation, otherwise no acetic acid is added when analyzing only alkylphenol compounds), flow rate 0.25 mL/min for 150 mm column and 0.4 mL for 250 mm column; gradient: 65% water proceeding to 90% acetonitrile over 25 or 35 min for 150 or 250 mm column, respectively, hold for 5 min, return to 65% water over 5 min, followed by 5 min at equilibrium; injection volume 5 μL (autosampler).

Tandem MS performed using triple-quadrupole MS (Waters-Micromass, Manchester, United Kingdom); nebulizer gas: nitrogen; collision gas: argon; capillary voltage: 3 kV in the positive mode and −2.8 kV in the negative mode; extractor lens: 1.0 V; RF lens 0.0 V; source and desolvation temperature: set at 80°C and 150°C, respectively, for syringe injection for MS/MS optimizations, and 120°C and 350°C under chromatographic HPLC conditions; cone gas flow: 50 L/h; desolvation gas flow: 600 L/h.

TABLE 25.1
Characteristic LC–MS/MS Parameters for Analysis of Endocrine Disrupting Metabolites of Nonionic Surfactants and Related Compounds

Compounds	Precursor Ion (*m/z*)	Cone Voltage (V)	Product Ions (*m/z*) (Collision Potential, eV)
Bisphenol A	227	45	133 (30), 212 (20)
4-Nonylphenol	219	45	133 (32), 147 (30)
4-*n*-Nonylphenol	219	40	106 (22)
4-*n*-Nonylphenol (d8)	227	45	112 (23)
4-Octylphenol	205	45	106 (20)
NPE1C	277	35	219 (18), 133 (40)
NPE1C (d2)	279	35	133 (40), 147 (40)
NPE2C	321	35	219 (20)
NPE3C	365	35	219 (20)
OPE1C	263	35	205 (20), 106 (30)
OPE2C	307	35	205 (20)
NPE1O	282 (+)	23	127 (10), 265 (7)
NPE1O (d2)	284 (+)	25	127 (9), 85 (15)
NPE2O	326 (+)	23	183 (12), 121 (23)
NPE3O	370 (+)	25	227 (12)
OPE1O	268 (+)	25	113 (10), 251 (7)
OPE2O	312 (+)	25	183 (12), 121 (23)

Notes: The number in the abbreviated form in the compound names is the total number of ethoxy groups present in the compound. Thus, NPE3O is the nonylphenol ethoxylate that contain two ethoxy units. The notation "d" represents the deuterated analog of the analyte used as internal standard.

Quantitative LC–MS/MS analysis is carried out in the multiple reaction monitoring (MRM) mode; argon pressure for collision-induced dissociation (CID): 3.5×10^{-3} mbar; collision energies 7–40 eV; specific parent ions: for alkylphenols, alkylphenol ethoxycarboxylates and bisphenol A, $[M - H]^-$, and for alkylphenol ethoxylates $[M + NH_4]^+$, respectively; MRM precursor–product ion pairs are monitored for quantification.

Compounds are identified from their characteristic precursor–product ions along with their RT. As mentioned above the alkylphenol ethoxylates, unlike their alkylphenols or ethoxycarboxylates counterparts, are identified as their NH_4^+ adduct ions, $[M + NH_4]^+$. Such ammonium adducts fragment easily and therefore, are better suited to detect alkylphenol ethoxylate-type compounds. Separate LC runs are recommended for analyzing ethoxylate compounds and the LC conditions specified in this foregoing procedure are eluant: acetonitrile–water (80:20), ammonium acetate 20 mM added to both; linear gradient: 35%–90% acetonitrile in 25 min, held for 5 min at 90% concentration, back to 35% concentration in 5 min, held 5 min for equilibrium. Presented in Table 25.1, are some characteristic parameters to identify and quantify the compounds as per the above procedure for LC–MS/MS analysis.

SPE–GC/MS Method

Aqueous sample, volume 100 mL is filtered through a prewashed 0.7 μm glass fiber filter (dried at 400°C for 4 h). NP and its ethoxylates are isolated from water on C-18 cartridges (fitted on a vacuum

apparatus). The cartridges are conditioned prior to their use, first with methanol using two portions of 3.5 mL each followed by 3 mL of reagent water twice at a flow rate of 0.5 mL/min. The samples are then passed through the cartridges at a flow rate of 10 mL/min. To remove any interference, the cartridges are washed with 2.5 mL reagent water four times and then dried under vacuum for 1 h. The compounds are then eluted from cartridges with methylene chloride–hexane (4:1) mixtures in 2 mL portion each four times. The eluates are evaporated to dryness at 40°C under a gentle stream of nitrogen. An amount of 50 mg of internal standard, such as, bisphenol A-d_{16} is then added into the vials. The internal standard solutions are similarly evaporated to dryness. NP and its ethoxylates are then subjected to derivatization reactions. For solid samples, extraction is carried out by sonication at 50°C for 30 min in 8 mL methanol–water mixture (5:3 v/v). The sample extract is centrifuged. The supernatant is collected and diluted with reagent water to a final volume of 100 mL. The compounds are then isolated from these diluted sample extracts by SPE steps outlined above.

The target compounds are derivatized with bis(trimethylsilyl)trifluoroacetamide in presence of pyridine. The latter acts as a catalyst in the derivatization reactions. For this, a volume of 50 μL of the derivatizing agent and 50 μL of pyridine are added into the vials containing dried residues of the sample and the internal standard. The contents are intimately mixed for 1 min in vials closed using a vortex system. The mixture is heated for 20 min at 65°C. The derivatives are cooled to room temperature for their analysis. The column and the conditions used in this procedure are as follows.

Column: DB-5, 60 m length, 0.25 um film thickness, and 0.32 mm ID; carrier gas: helium at a constant flow rate of 0.9 mL/min; temperature: oven, 80°C for 1 min, 15°C/min from 80°C to 220°C, 5°C/min from 220°C to 280°C; injector 280°C, MS transfer line 280°C and ion source 180°C; injection volume 1 μL in split-less mode; MS mass range for full scan mode 50–400. Quantification is performed under SIM mode choosing the following ions to identify and quantify.

4-*n*-NP: 179 and 292
NP1EO: 237, 251, 265, 293
NP2EO: 309, 295
TCS: 200, 247, 362
Bisphenol A d-16 (internal standard): 368, 369
Bisphenol A: 357, 358

The mono- and diethoxylates are isomeric mixtures producing several peaks. The sums of the areas of such peaks are used for quantification, respectively. The compounds furthermore are identified from their RTs in addition to their characteristic mass ions.

Arditsoglou and Voutsa (2008) have proposed a similar GC/MS analytical procedure to measure phenolic and steroid endocrine disrupting compounds in environmental matrices. The target compounds are analyzed by GC/MS as derivatives of *N*,*O*-bis(trimethylsilyl)trifluoroacetamide. The efficacy of various SPE cartridges including Oasis HLB, C-18, Florisil, silica, and combination of silica and alumina in separation and preconcentration of these compounds have been reported. The solvents used in this study were acetone, methanol, acetone–methanol mixture (1:1), and ethyl acetate. The latter two solvents showed better efficiency. In solid analysis, ultrasonic-assisted extraction gives satisfactory recoveries of target compounds, however, an additional sample cleanup step is needed.

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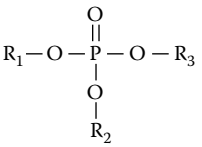
26 Emerging Pollutants
Organophosphate Flame Retardants, Plasticizers, and Lubricants

Organophosphate esters constitute an important class of emerging pollutants. In recent years, these substances have found numerous applications for diverse purposes. One of the most important applications involve their use as flame retardant additives in textiles, varnishes, woods, carpets, wall coverings, building materials, furniture, electronic equipment, and several polymers to inhibit the combustion process. In addition, these substances are extensively used as plasticizers, stabilizers, and wetting agents. They are also used as antifoaming agents in lubricants and hydraulic fluids. As additives, these substances are normally dispersed or physically mixed into the materials and not chemically bonded. Since they are not bound chemically into the bulk materials these compounds are susceptible to leach out readily into the aquatic environment such as wastewater, groundwater, effluent water from sewage treatment plants, as well as into the nonaquatic environment including hazardous waste sites, soils, sediments, and indoor air. Among the organophosphorus compounds that are widely used in a multitude of applications, phosphate esters are the most common ones. However, different groups of organophosphorus compounds, such as phosphonates and phosphites, are also used in different applications. Relatively high concentrations of some organophosphate esters have been detected in rivers in the United States and Central Europe (Andresen et al., 2004; Fries and Puttmann, 2001; Glassmeyer et al., 2005). They have been found in wastewater samples (Fries and Puttmann, 2003) and indoor air (Marklund et al., 2003, 2005; Staaf and Ostman, 2005).

The organophosphates have the following structural features:



where *P* is bound to four O atoms, one of which is a double bond, and R_1, R_2, and R_3 are alkyl or aryl groups. For example, in the chemical structure of di-*n*-butyl phosphate, $R_1{=}R_2{=}R_3$, that is, each O atom attached to the P atom by a single bond is also attached to a butyl group (CH_3–CH_2–CH_2–CH_2–). Similarly, in 2-ethylhexyldiphenyl phosphate, while one of the alkyl group, say R_1 is the 2-ethylhexyl group (CH_3–CH_2–CH_2–CH_2–CH_2 (–CH_2–CH_3)–CH_2–), the other two, R_2 and R_3 are two phenyl (C_6H_5–) groups, respectively. Table 26.1 presents some selected compounds of this class with their abbreviated names, molecular formulas, and Chemical Abstract Service (CAS) registry numbers. The vapor pressure of these compounds and their log K_{ow} (octanol–water partition coefficient) data (Reemtsma et al., 2008) are also presented in this table.

Several analytical procedures have been described in the literature to measure organophosphates in environmental matrices. Some of these procedures to measure trace organophosphates, both chlorinated and nonchlorinated compounds, are briefly outlined below. Such methods usually employ liquid–liquid extraction or solid-phase extraction. In addition, microextraction techniques

TABLE 26.1
Names, Formulas, CAS Numbers, K_{ow} and Vapor Pressure Values of Some Organophosphate Compounds

Compounds	Formulae	CAS No.	Log K_{ow}	Vapor Pressure (Torr)
Trimethyl phosphate (TMP)	$C_3H_9O_4P$	512-56-1	−0.65	8.50×10^{-1}
Triethyl phosphate (TEP)	$C_6H_{15}O_4P$	78-40-0	0.80	3.93×10^{-1}
Tripropyl phosphate (TPrP)	$C_9H_{21}O_4P$	513-08-6	1.87	4.33×10^{-3}
Tri-*n*-butyl phosphate (TnBP)	$C_{12}H_{27}O_4P$	126-73-8	4.00	1.13×10^{-3}
Tri-iso-butyl phosphate (TiBP)	$C_{12}H_{27}O_4P$	126-71-6	3.60	1.28×10^{-2}
Tributoxyethyl phosphate (TBEP)	$C_{18}H_{39}O_7P$	78-51-3	3.75	2.50×10^{-8}
Triphenyl phosphate (TPhP)	$C_{18}H_{15}O_4P$	115-86-6	4.59	6.28×10^{-6}
Tricresyl phosphate (TCrP)	$C_{21}H_{21}O_4P$	1330-78-5	5.11	6.00×10^{-7}
Tri(2-ethylhexyl) phosphate (TEHP)	$C_{24}H_{51}O_4P$	78-42-2	9.49	8.45×10^{-8}
Di-*n*-butyl phosphate (DnBP)	$C_8H_{19}O_4P$	107-66-4	2.29	4.26×10^{-9}
Di(2-ethylhexyl) phosphate (DEHP)	$C_{16}H_{35}O_4P$	298-07-7	6.07	4.65×10^{-8}
Mono(2-ethylhexyl) phosphate (MEHP)	$C_8H_{19}O_4P$	12645-31-7	2.65	5.34×10^{-7}
2-Ethylhexyldiphenyl phosphate (EHDPP)	$C_{20}H_{27}O_4P$	856800-52-7	6.64	6.49×10^{-7}
Tri(2-chloroethyl) phosphate (TCEP)	$C_6H_{12}Cl_3O_4P$	115-96-8	1.44	6.13×10^{-2}
Tri(chloropropyl) phosphate (TCPP)	$C_9H_{18}Cl_3O_4P$	13674-84-5	2.59	2.02×10^{-5}
Tri(dichloropropyl) phosphate (TDCP)	$C_9H_{15}Cl_6O_4P$	13674-87-8	3.65	7.36×10^{-8}

are also being developed to reduce the consumption of organic solvents and for certain substances to improve the selectivity of their extractions. Microwave-assisted extraction methods are suitable for indoor air dust samples. The compounds in the solvent extracts may be determined by GC-NPD, GC/MS, LC/MS, or other techniques.

Martinez-Carballo et al. (2007) have described an analytical procedure to measure selected organophosphate esters in water and sediments. The method involves liquid–liquid extraction for aqueous samples and ultrasound-assisted solvent extraction for sediment samples. Aqueous samples were extracted with methylene chloride after adjusting the pH to 7. The extracts were concentrated down to a small volume and solvent exchanged with acetonitrile for analyses. The sediment samples were subjected to ultrasound-assisted solvent extractions for 30 min with ethyl acetate–acetonitrile mixtures (30:70 by volume). The solvent extract was centrifuged and evaporated under a stream of nitrogen and then the final volume adjusted to 1 mL with acetonitrile. The phosphate esters were analyzed by LC–tandem MS (LC–MS/MS). The compounds were separated on a 150 mm × 2 mm (5-um particle) C-8 HPLC column. The spike recoveries of these substances to determine the accuracy of the method ranged from 63% to 93% for waters while 74% to 104% for sediment samples, respectively.

Andresen and Bester (2006) have described a method to purify the organophosphate esters, flame retardants, and plasticizers in drinking water and their trace analysis. The analytical procedure involves extracting 1 L of water with 10 mL toluene under vigorous stirring for 30 min with a teflonized magnetic stirrer. The mixture is allowed to stand for 20 min to separate the top toluene layer from the aqueous phase. To remove any trace water that may be present, the solvent extract is subjected to freezing at a temperature of −20°C overnight. The volume of the solvent extract is then reduced to 1 mL by heating at 60°C at a pressure of 45 Torr. The compounds are analyzed by GC/MS equipped with the PTV injector with a sintered glass liner for large volume injection (40 μL). The GC and MS conditions used in this method are as follows:

TABLE 26.2
Characteristic Mass Ions of Selected Organophosphates for GC/MS Analysis

Phosphate Esters	Primary Mass Ion (amu)	Secondary Mass Ion (amu)
Tri-iso-butyl phosphate (TiBP)	211	155
Tri-*n*-butyl phosphate (TnBP)	211	155
Tri(2-chloroethyl) phosphate (TCEP)	249	251
Tri(2-chloro-1-methylethyl) phosphate (TCPP)	277	279
Tri(2-chloro-1-chloromethylethyl) phosphate (TDCP)	379	381
Tri(butoxyethyl) phosphate (TBEP)	199	299
2-Ethylhexyldiphenyl phosphate (EHDPP)	251	362
Triphenyl phosphate (TPP)	325	326

GC column and conditions: Column DB-5 (J&W Scientific, Folsom, California), length 15 m, ID 0.25 mm, film 0.25 um; temperature: 100°C, 30°C/min to 130°C, 8°C/min to 220°C, 30°C/min to 280°C, 7 min; carrier gas: helium, flow rate 1.3 mL/min; injection volume 40 μL.

MS conditions: electron impact ionization, electron energy 70 eV, operated in selected ion monitoring (SIM) mode. The primary and secondary characteristic mass ions for identification and quantification are given in Table 26.2. TnBP-D27 and TPP-D15 were used as internal standards in this study.

Garcia-Lopez et al. (2007a,b) have described a dispersive liquid–liquid microextraction (DLLME) technique for extracting several phosphate esters from waters for their analysis by GC-NPD. In this procedure, a salt solution of the sample (20% sodium chloride) is used for extraction. A 10 mL volume of this sample salt solution is placed in a 12 mL conic bottom glass tube with a screw cap and polytetrafluoroethylene (PTFE)-lined septum. To this solution is added 1 mL of acetone–trichloroethane extractant solution made from mixing 1 mL of acetone and 20 μL of 1,1,1-trichloroethane. The mixture is allowed to stand for 1 min. The closed tube is then centrifuged at 3500 rpm for 3 min. The dispersed droplet of trichloroethane settles at the bottom of the tube during this centrifugation. The volume of the droplet builds up to about 12 μL. Most of the supernatant water is removed from the tube with a Pasteur pipet. A 2 μL volume of the extract is then injected onto the GC equipped with a split/splitless injector and a NPD system. The phosphate esters are separated on the GC column and detected with the NPD under P mode. The column and the conditions used in this procedure are as follows.

Column: DB-5 type (5% phenyl, 95% methylpolysiloxane) capillary column, 30 m × 0.32 mm ID × 0.25 um thickness; oven temperature, 70°C (1 min), first ramp at 15°C/min to 200°C (3 min), second ramp at 5°C/min to 250°C (5 min), for extracts in chlorobenzene the initial oven temperature should be 100°C; injector temperature 270°C; carrier and auxillary gas (for NPD system), nitrogen (99.999%).

Garcia-Lopez et al. (2008) also described a different type of liquid–liquid microextraction procedure using polypropylene microporous membranes. This procedure involves dipping 2 cm long polypropylene membranes containing about 7 μL of octanol in the pores in a glass vial filled with 115 mL water and 30% sodium chloride. The solution mixture is stirred at room temperature for 12 h using a magnetic stirrer. The organophosphates are then recovered from the membrane with 0.2 mL ethyl acetate. An internal standard, triphenyl phosphate (50 μL) solution in ethyl acetate is then mixed with the extract for GC analysis using NPD. The extract may be further concentrated to enhance the enrichment factor.

Solid-phase microextraction methods have been described as an attractive alternative to the liquid–liquid microextraction. Such techniques are known to measure organophosphorus pesticides.

Rodriguez et al. (2006) have described one such procedure to determine organophosphate flame-retardants and plasticizers of a wide range of polarity in water samples. The extraction is carried out at ambient temperature for 40 min using 22 mL glass vials with a magnetic stir bar. The vials are filled completely with sample aliquots containing 300 mg/L NaCl. The pH range of the sample should fall in the range of 6–8. The analytes are concentrated on a polydimethylsiloxane (PDMS)–divinylbenzene (DVB) fiber. The fibers are desorbed at 270°C for 5 min in the splitless mode. The compounds are measured by GC-NPD.

ANALYSIS OF INDOOR DUST

Organophosphate flame retardants and plasticizers may often be found in the environment in indoor dust samples. Their extractions and analyses are described in detail (Garcia-Lopez et al., 2007a,b; Marklund et al., 2003). The dust samples are collected from dust bags of conventional vacuum cleaners or by wipe tests. The samples are transferred with tweezers to clean glass jars, covered with aluminum foil and Teflon lined lids, and stored in a freezer prior to extraction. The samples may be extracted by either ultrasonication or by Soxhlet extraction. Ultrasonication proves to be a better extraction technique over the Soxhlet extraction (Marklund et al. 2003). In ultrasonication, 1–2 g of samples placed in a 100 mL beaker are extracted twice with 25 mL dichloromethane at room temperature for 20 min in an ultrasonic bath. The extracts are filtered, rinsed with the same solvent, and evaporated down to a small volume under nitrogen and GC-NPD.

Indoor dust samples and airborne particles may also be extracted under heating in a microwave oven using an appropriate solvent. One such procedure describes extraction at 130°C (Garcia-Lopez et al., 2007a). Acetone is reported to be the most efficient solvent. The method, however, requires intensive cleanup steps involving dilution with ultrapure water, concentration on a reversed-phase sorbent, and further purification using silica. The purified solvent extract is analyzed by GC-NPD.

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27 Emerging Pollutants *Pharmaceuticals and Personal Care Products*

There has been a growing concern in recent years because several pharmaceutical and personal care products (PPCPs) are being found in the environmental matrices. These substances enter into the environment from their widespread use and uncontrolled release. Many such substances are being found at trace concentrations in water, soil, sediments, and biosolids. Several analytical methods have been developed and described in the literature to determine these substances in environmental matrices (Castiglioni et al., 2005; Kasprzyk-Horden et al., 2008; Kolpin et al., 2002; Lindsay et al., 2001; Rice and Mitra, 2007; Vanderford et al., 2003). The U.S. EPA Method 1694 (2007) describes an analytical method to measure these substances in multimedia environmental samples by HPLC combined with tandem MS (HPLC/MS/MS). A number of such compounds may also be analyzed by other instrumental techniques; the HPLC/MS/MS technique, however, is commonly employed because it gives lower detection limits with authentic identifications. The U.S. EPA Method 1694 is discussed below in brief. This method has been developed for use as required for monitoring these pollutants under the Clean Water Act of the U.S. EPA.

U.S. EPA METHOD 1694

Summary of the Method

This method is used for qualitative and quantitative determination of a total of 74 PPCPs by HPLC/MS/MS. These analytes are listed alphabetically in Table 27.1 with their CAS registry numbers. The method is used to determine the target compounds in drinking water, wastewater, groundwater, dry and wet soils, sediments, filter cakes, compost, untreated effluents, and municipal sludge. The analytical procedure may also be applied to measure these compounds in other matrices. The analytical procedure involves the following steps: (1) sample preparation/extraction, pH adjustment, and spiking labeled standards, (2) sample cleanup with SPE cartridges, (3) LC–MS/MS run, (4) compounds identification, and (5) quantification.

The target compounds in this method are divided into four groups and each group is analyzed in separate LC–MS/MS runs. The Group 1 and 2 compounds are extracted under an acidic medium at pH 2 and analyzed in the positive ESI mode (ESI+). The LC conditions for these groups, however, differ. The instrument conditions for measuring the compounds of Group 1 are shown in Table 27.2. In Table 27.3, their RTs, the *m/z* of the parent–daughter transitions, and the labeled analogs or the internal standards used for quantifications are listed. Likewise, for the Group 2 compounds, the instrument and the analytical conditions are listed in Tables 27.4 and 27.5, respectively. The compounds of Group 3, unlike those in Groups 1 and 2 are run in the negative ESI (ESI−) mode. The instrument conditions for this group are listed in Table 27.6 and their RTs, and parent–daughter transitions and the quantifying references are presented in Table 27.7, respectively. The compounds classified in Group 4, unlike the first three groups are extracted under basic conditions at the pH 10. They are analyzed in the ESI+ mode. The instrument conditions and the markers for qualitative identifications and quantification for this group are shown in Tables 27.8 and 27.9, respectively.

TABLE 27.1
Names and CAS Registry Numbers for PPCPs Determined by Isotope Dilution and Internal Standard HPLC/MS/MS

Compound	CAS Registry Number	Labeled Analog
Acetaminophen	103-90-2	$^{13}C_{2}$-^{15}N-Acetaminophen
Albuterol	18559-94-9	Albuterol-d_3
Ampicillin	69-53-4	
Anhydrochloretatercycline (ACTC)	4497-O8-9	
Andytrotetracycline (ATC)	4496-85-9	
Azithromycin	83905-01-5	
Caffeine	58-08-2	$^{13}C_3$-Caffeine
Carbadox	68O4-07-5	
Carbamazepine	298-46-4	
Cefotaxime	63572-52-6	
Chlortetracycline (CTC)	57-62-5	
Cimetidine	51481-61-9	
Ciprofloxacin	85721-33-1	$^{13}C_3$–15_N-Ciprofloxacin
Clarithromycin	81103-11-9	
Clinafloxacin	105956-97-6	
Cloxacillin	61-72-3	
Codeine	76-57-3	
Cotinine	486-56-6	Cotinine-d_3
Dehydronifedipine	67035-22-7	
Demeclocycline	127-33-3	
Digoxigenin	1672-46-4	
Digoxin	20830-75-5	
Dilitazem	42399-41-7	
1,7-Dimethylxanthine	611-59-6	
Diphenhydramime	58-73-1	
Doxycycline	564-25-0	
Enrofloxacin	93106-60-6	
4-Epianhydrochlortetracycline (EACTC)	158018-53-2	
4-Epianhydrotetracycline (EATC)	4465-65-0	
4-Epichlortetracycline (ECTC)	14297-93-9	
4-Epioxytetracycline (EOTC)	14206-58-7	
4-Epitetracycline (ETC)	23313-80-6	
Erythromycin	114-07-8	
Erythromycin anhydrate	59319-72-1	$^{13}C_2$-Erythromycin anhydrate
Flumequine	42835-25-6	
Fluoxetine	54910-89-3	Fluoxetine-d_3
Gemfibrozil	25812-30-0	Gemfibrozil-d_6
Ibuprofen	15687-27-1	$^{13}C_3$-Ibuprofen
Isochlortetracycline (ICTC)	514-53-4	
Lincomycin	154-21-2	
Lomefloxacin	98079-51-7	
Metformin	657-24-9	Metformin-d_6
Miconazole	22916-47-8	
Minocycline	10118-91-8	
Naproxen	22204-53-1	^{13}C-Naproxen-d_3
Norfloxacin	70458-96-7	

(*Continued*)

TABLE 27.1 (*Continued*)
Names and CAS Registry Numbers for PPCPs Determined by Isotope Dilution and Internal Standard HPLC/MS/MS

Compound	CAS Registry Number	Labeled Analog
Norgestimate	35189-28-7	
Ofloxacin	82419-36-1	
Ormetoprim	6981-18-6	
Oxacillin	66-79-5	
Oxolinic acid	14698-29-4	
Oxytetracycline (OTC)	79-57-2	
Penicillin V	87-08-1	
Penicillin G	61-33-6	
Ranitidine	66357-35-5	
Roxithromycin	80214-83-1	
Sarafloxacin	98105-99-8	
Sulfachloropyridazine	80-32-0	
Sulfadiazine	68-35-9	
Sulfadimethoxine	122-11-2	
Sulfamerazine	127-79-7	
Sulfamethazine	57-68-1	$^{13}C_6$-Sulfamethazine
Sulfamethizole	144-82-1	
Sulfamethoxazole	723-46-6	$^{13}C_6$-Sulfamethoxazole
Sulfanilamide	63-74-1	
Sulfathiazole	72-14-0	
Tetracycline (TC)	60-54-8	
Thiabendazole	148-79-8	Thiabendazole-d_6
Triclocarban	101-20-2	$^{13}C_6$-Triclocarban
Triclosan	3380-34-5	$^{13}C_{12}$-Triclosan
Trimethoprim	738-70-5	$^{13}C_3$-Trimethoprim
Tylosin	1401-69-0	
Virginiamycin	1106-76-1	
Warfarin	81-81-2	Warfarin-d_5
Other Standards		
Unlabeled compound spiked into sample and used for recovery correction		
Meclocycline		
Labeled injection internal standard spiked into sample extract prior to injection into LC–MS/MS		
		$^{13}C_3$-Atrazine
		$^{13}C_6$-2,4,5-Trichlorophenoxyacetic acid ($^{13}C_6$-TCPAA)

SAMPLE PREPARATION

If the sample is aqueous, take two aliquots of volume 1 L each and adjust the pH to 2 and 10, respectively, by adding an acid or a base. Isotopically stable labeled analogs of the selected analytes are then added into their respective acid and the base fractions. Such labeled analogs are employed in this method because many compounds are quantified by the isotope dilution technique. The acid fraction of the sample is then stabilized by adding tetrasodium ethylenediamine tetraacetate dihydrate ($Na_4 \cdot EDTA \cdot 2H_2O$) into it. If the sample is a solid, biosolid, or a semisolid, use an amount of 1 g measured as dry weight or as dry solid filtered from an aqueous sample for the analysis.

TABLE 27.2
Group 1 Compounds: LC Gradient and MS Conditions (Acidic Extractions and ESI+)

LC Gradient Program			
Time (min)	**Flow Mixture**	**LC Flow Rate (mL/min)**	**Gradient**
0.0	Solvents A/B (95:5%)	0.150	1
4.0	Solvents A/B (95:5%)	0.250	6
22.5	Solvents A/B (12:88%)	0.300	6
23.0	Solvent B (100%)	0.300	6
26.0	Solvent B (100%)	0.300	6
26.5	Solvents A/B (95:5%)	0.150	6
33.0	Solvents A/B (95:5%)	0.150	6

Notes: Solvent A = 0.3% formic acid and 0.1% ammonium formate in HPLC water.
Solvent B = acetonitrile–methanol (1:1).
General LC conditions: column temperature 40°C; flow rate 0.20–0.23 mL/min; maximum pressure 345 bar; auto-sampler tray temperature 4°C; injection volume 5 µL.
MS conditions: source temperature 120°C; desolvation temperature 400°C; cone/desolvation gas rate 70 L/h/450 L/h.

TABLE 27.3
Group 1 Acidic Extraction, ESI+ Compound RTs, Parent–Daughter Transitions, Quantitation References, Method Detection Limits, and Minimum Levels of Quantitations

Analyte	**RT (min)**	**Parent–Daughter (*m/z*s)**	**Quantitation Reference**
		Native Compounds	
Sulfanilamide	2.5	190.0–155.8	$^{13}C_6$-Sulfamethazine
Cotinine	2.8	177.0–98.0	Cotinine-d_3
Acetaminophen	4.6	152.2–110.0	$^{13}C_{2-}{}^{15}$N-Acetaminophen
Sulfadiazine	6	251.2–156.1	$^{13}C_6$-Sulfamethazine
1,7-Dimethylxanthine	6.9	181.2–124.0	$^{13}C_3$-Caffeine
Sulfathiazole	7.7	256.3–156.0	$^{13}C_6$-Sulfamethoxazole
Codeine	8.3	300.0–152.0	$^{13}C_3$-Timethoprim
Sulfamerazine	8.7	265.0–156.0	$^{13}C_6$-Sulfamethazine
Lincomycin	9.3	407.5–126.0	$^{13}C_3$-Timethoprim
Caffeine	9.3	195.0–138.0	$^{13}C_3$-Caffeine
Sulfamethizole	10	271.0–156.0	$^{13}C_6$-Sulfamethoxazole
Trimethoprim	10	291.0–230.0	$^{13}C_3$-Timethoprim
Thiabendazole	10	202.1–175.1	Thiabendazole-d_6
Sulfamethazine	10.1	279.0–156.0	$^{13}C_6$-Sulfamethazine
Cefotaxime	10.2	456.4–396.1	$^{13}C_3$-Timethoprim
Carbadox	10.5	263.2–231.2	$^{13}C_3$-Timethoprim
Ormetoprim	10.5	275.3–259.1	$^{13}C_3$-Timethoprim
Norfloxacin	10.7	320.0–302.0	$^{13}C_3$ ^{15}N-Ciprofloxacin
Sulfachloropyridazine	10.8	285.0–156.0	$^{13}C_6$-Sulfamethazine
Ofloxacin	10.8	362.2–318.0	$^{13}C_3$ ^{15}N-Ciprofloxacin

(*Continued*)

TABLE 27.3 (*Continued*)
Group 1 Acidic Extraction, ESI+ Compound RTs, Parent–Daughter Transitions, Quantitation References, Method Detection Limits, and Minimum Levels of Quantitations

Analyte	RT (min)	Parent–Daughter (*m/z*s)	Quantitation Reference
Ciprofloxacin	10.9	332.2–314.2	$^{13}C_3$ ^{15}N-Ciprofloxacin
Sulfamethoxazole	11.2	254.0–156.0	$^{13}C_6$-Sulfamethoxazole
Lomefloxacin	11.2	352.2–308.1	$^{13}C_3$ ^{15}N-Ciprofloxacin
Enrofloxacin	11.5	360.0–316.0	$^{13}C_3$ ^{15}N-Ciprofloxacin
Sarafloxacin	11.9	386.0–299.0	$^{13}C_3$ ^{15}N-Ciprofloxacin
Clinafloxacin	12.1	366.3–348.1	$^{13}C_3$ ^{15}N-Ciprofloxacin
Digoxigenin	12.6	391.2–355.2	$^{13}C_3$-Timethoprim
Oxolinic acid	13.1	261.8–243.8	$^{13}C_3$-Timethoprim
Sulfadimethoxine	13.2	311.0–156.0	$^{13}C_6$-Sulfamethoxazole
Diphenhydramime	14.5	256.8–168.1	$^{13}C_3$-Timethoprim
Penicillin G	14.6	367.5–160.2	$^{13}C_3$-Timethoprim
Azithromycin	14.8	749.9–591.6	$^{13}C_3$-Timethoprim
Flumeqine	15.2	262.0–173.7	$^{13}C_3$-Timethoprim
Ampicillin	15.3	350.3–160.2	$^{13}C_3$-Timethoprim
Diltiazem	15.3	415.5–178.0	$^{13}C_3$-Timethoprim
Carbamazepine	15.3	237.4–194.2	$^{13}C_3$-Timethoprim
Penicillin V	15.4	383.4–160.2	$^{13}C_3$-Timethoprim
Erythromycin	15.9	734.4–158.0	$^{13}C_2$-Erythromycin
Tylosin	16.3	916.0–772.0	$^{13}C_2$-Erythromycin anhydrate
Oxacillin	16.4	434.3–160.1	$^{13}C_3$-Timethoprim
Dehydronifedipine	16.5	345.5–284.1	$^{13}C_3$-Timethoprim
Digoxin	16.6	803.1–283.0	$^{13}C_3$-Timethoprim
Fluoxetine	16.9	310.3–148.0	Fluoxetine-d_5
Cloxcillin	16.9	469.1–160.1	$^{13}C_3$-Timethoprim
Virginiamycin	17.3	508.0–355.0	$^{13}C_3$-Timethoprim
Clarithromycin	17.5	748.9–158.2	$^{13}C_2$-Erythromycin anhydrate
Erythromycin anhydrate	17.7	716.4–158.0	$^{13}C_2$-Erythromycin anhydrate
Roxithromycin	17.8	837.0–679.0	$^{13}C_2$-Erythromycin anhydrate
Miconazole	20.1	417.0–161.0	$^{13}C_3$-Timethoprim
Norgestimate	21.7	370.5–124.0	$^{13}C_3$-Timethoprim
	Labeled Compounds Spiked into Each Sample		
Cotinine-d_3	2.8	180.0–79.9	$^{13}C_3$ Atrazine
$^{13}C_2$-^{15}N-Acetaminophen	4.5	155.2–111.0	$^{13}C_3$ Atrazine
$^{13}C_3$ Caffeine	9.3	198.0–140.0	$^{13}C_3$ Atrazine
Thiabendazole-d_6	9.8	208.1–180.1	$^{13}C_3$ Atrazine
$^{13}C_3$-Timethoprim	10	294.0–233.0	$^{13}C_3$ Atrazine
$^{13}C_6$ Sulfamethazine	10.1	285.1–162.0	$^{13}C_3$ Atrazine
$^{13}C_3$^{15}N-Ciprofloxacin	10.9	336.1–318.0	$^{13}C_3$ Atrazine
13C6-Sulfamethoxazole	11.2	260.0–162.0	$^{13}C_3$ Atrazine
$^{13}C_2$-Erythromycin	15.9	736.4–160.0	$^{13}C_3$ Atrazine
Fluoxetine-d_5	16.8	315.3–153.0	$^{13}C_3$ Atrazine
$^{13}C_2$-Erythromycin anhydrate	17.7	718.4–160.0	$^{13}C_3$ Atrazine
	Injection Internal Standard		
$^{13}C_3$ Atrazine	15.9	219.5–176.9 (134.0)	External standard

TABLE 27.4
Group 2 Compounds: LC Gradients and MS Conditions (Acidic Extraction and ESI+)

LC Gradient Program			
Time (min)	**Flow Mixture**	**LC Flow Rate (mL/min)**	**Gradient**
0.0	Solvents A/B (10:90%)	0.20	1
1.0	Solvents A/B (10:90%)	0.20	6
18.0	Solvents A/B (40:60%)	0.23	6
20.0	Solvents A/B (90:10%)	0.23	6
24.0	Solvents A/B (90:10%)	0.23	6
24.3	Solvents A/B (10:90%)	0.20	6
28.0	Solvents A/B (10:90%)	0.20	6

Notes: Solvent A = acetonitrile/methanol (1:1).
Solvent B = aqueous solution of oxalic acid, 5 mM in HPLC grade water.
General LC conditions: column temperature 40°C; flow rate 0.20–0.23 mL/min; maximum pressure 345 bar; auto-sampler tray temperature 4°C; injection volume 5 µL.
MS conditions: source temperature 120°C; desolvation temperature 400°C; cone/desolvation gas rate 70 L/h/450 L/h.

TABLE 27.5
Group 2 Compounds: RTs and Parent–Daughter Transitions (ESI+ and Acidic Extraction)

Native Compounds	**RT (min)**	**Parent–Daughter (*m/z*)**
Minocycline	5.1	458.0–441.0
Epitetracycline	8.1	445.2–410.2
Epioxytetracycline	8.6	461.2–426.2
Oxytetracycline	9.4	461.2–426.2
Tetracycline	9.9	445.2–410.2
Demeclocycline	11.7	465.0–430.0
Isochlortetracycline	11.9	479.0–462.2
Epichlortetracycline	12.0	479.0–444.0
Chlortetracycline	14.1	479.0–444.0
Doxycycline	16.7	445.2–428.2
Epianhydrotetracycline	17.0	426.8–409.8
Anhydrotetracycline	18.8	426.8–409.8
Epianhydrochlortetracycline	20.7	461.2–444.0
Anhdrochlortetracycline	22.1	461.2–444.0
Thiabendazole-d_6 (Reference)	7.0	208.1–180.1
$^{13}C_3$ Atrazine (IS)	10.5	219.5–176.9

Notes: Thiabenzadole-d_6 is used as a reference standard for quantitation.$^{13}C_3$ Atrazine is used as the internal standard. Isochlortetracycline is reported combined with epichlortetracycline due to common transition ion.

TABLE 27.6
Group 3 Compound: LC Gradient and MS Conditions (Acidic Extraction and ESI−)

LC Gradient Program			
Time (min)	**Flow Mixture**	**LC Flow Rate (mL/min)**	**Gradient**
0.0	Solvents A/B (60%/40%)	0.2	1
0.5	Solvents A/B (60%/40%)	0.2	6
7.0	Solvent B (100%)	0.2	6
12.5	Solvent B (100%)	0.2	6
12.7	Solvents A/B (60%/40%)	0.2	6
16.0	Solvents A/B (60%/40%)	0.2	1

Notes: Solvent A = 0.1% ammonium acetate and 0.1% acetic acid in HPLC grade water.
Solvent B = methanol/acetonitrile (1:1).
General LC conditions: column temperature 40°C; flow rate 0.200 mL/min; maximum pressure 345 bar; auto-sampler tray temperature 4°C; injection volume 15 µL.
MS conditions: source temperature 100°C; desolvation temperature 350°C; cone/desolvation gas rate 50 L/h/300 L/h.

Take two aliquots of the sample 1 g each. While one aliquot of this solid sample is adjusted to an acidic pH with a phosphate buffer, the other aliquot is made basic with ammonium hydroxide. The acid fraction is stabilized with $Na_4 \cdot EDTA \cdot 2H_2O$. The labeled compounds are then spiked into their respective acid and base fractions. They are then extracted ultrasonically. The acid fraction is mixed with 20 mL acetonitrile, sonicated for 30 min, and centrifuged for about 5 min at 3000 rpm. Decant the supernatant extract and add 15 mL of phosphate buffer and adjust the pH between 1.95 and 2.05. Perform a second extraction of the solid residues repeating the above steps and a third extraction only with 15 mL of acetonitrile solution and combine all the extracts. The base fraction is similarly extracted thrice as outlined above, however, with the pH being adjusted between 9.95 and 10.05 by adding ammonium hydroxide dropwise. The solutions are concentrated to remove acetonitrile and diluted with reagent water.

SAMPLE CLEANUP

The acid and the base fractions of the aqueous samples or the aqueous extracts of the solid samples prepared above are cleaned up separately by SPE with HLB cartridges. Assemble the SPE extraction apparatus and condition the HLB cartridges by eluting with 20 mL methanol and 6 mL reagent water. For acid fractions, the cartridges should be further eluted with 6 mL reagent water at pH 2. The sample fractions are loaded onto the cartridges and eluted at a flow rate of 5–10 mL/min. Acid fraction cartridge is washed with 10 mL reagent water to remove the EDTA. Base fraction cartridge need not be washed. Dry the cartridges for either fraction under vacuum for approximately 5 min. Acid fraction analytes are eluted from the cartridges with 12 mL methanol first using vacuum and then under gravity. If triclosan and triclocarban that are to be analyzed elute these two compounds with 6 mL acetone–methanol (1:1). The base fraction is eluted with 6 mL methanol followed by 2% formic acid solution.

LC–MS/MS ANALYSIS

The operating conditions for analyzing samples should be the same as that for calibration standards. The analysis is performed in ESI+ mode for the acid fraction Groups 1 and 2 and for base fraction

TABLE 27.7
Group 3 Compounds: RTs and Parent–Daughter Transitions (Acidic Extraction and ESI−)

Native Compounds	RT (min)	Parent–Daughter (*m/z*)	Quantitation Reference
Naproxen	6.7	228.9–168.6	^{13}C-Naproxen-d_3
Warfarin	7.1	307.0–117.0	Warfarin-d_5
Ibuprofen	8.4	205.2–161.1	$^{13}C_3$-Ibuprofen
Gemfibrozil	9.5	249.0–121.0	Gemfibrozil-d_6
Triclocarbon	9.6	312.9–159.7	$^{13}C_6$-Triclocarbon
Triclosan	9.7	286.8–35.0	$^{13}C_{12}$-Triclosan
^{13}C-Naproxen-d_3	6.6	232.9–168.6	$^{13}C_6$-TCPAA
Warfarin-d_5	7.0	312.0–161.0	$^{13}C_6$-TCPAA
$^{13}C_3$-Ibuprofen	8.5	208.2–163.1	$^{13}C_6$-TCPAA
Gemfibrozil-d_6	9.5	255.0–121.0	$^{13}C_6$-TCPAA
$^{13}C_6$-Triclocarbon	9.6	318.9–159.7	$^{13}C_6$-TCPAA
$^{13}C_{12}$-Triclosan	9.7	298.8–35.0	$^{13}C_6$-TCPAA
$^{13}C_6$-TCPAA (IS)	4.9	258.8–200.7	External standard

Notes: The labeled compounds are spiked into the sample to quantify their unlabeled counterparts.
$^{13}C_6$-TCPAA is the internal standard used to quantify the labeled compounds above.

Group 4 compounds. The Group 3 compounds are run in ESI− mode. The instrument and conditions used in this foregoing method are as follows. The general LC conditions and the gradient program are listed in the tables for Groups 1–4.

Instrument: Waters 2690 HPLC or Waters 2795 HPLC, Micromass Quattro Ultima MS/MS
LC Column: Waters Xtera C18, 10.0 cm, 2.1 mm i.d., 3.5 um particle size
Ionization: Positive ion electrospray/negative ion electrospray
MS source temperature: 140°C
MS desolvation temperature: 350°C

TABLE 27.8
Group 4 Compound: LC Gradient and MS Conditions (Basic Extraction and ESI+)

LC Gradient Program			
Time (min)	**Flow Mixture**	**LC Flow Rate (mL/min)**	**Gradient**
0.0	Solvents A/B (2%/98%)	0.25	1
5.0	Solvents A/B (30%/70%)	0.25	6
12.0	Solvents A/B (30%/70%)	0.25	6
12.5	Solvents A/B (2%/98%)	0.25	6
16.0	Solvents A/B (2%/98%)	0.25	6

Notes: Solvent A = 0.1% acetic acid/ammonium acetate buffer.
Solvent B = acetonitrile.
General LC conditions: column temperature 40°C; flow rate 0.25 mL/min; maximum pressure 345 bar; autosampler tray temperature 4°C; injection volume 2 µL.
MS conditions: source temperature 120°C; desolvation temperature 350°C; cone/desolvation gas rate 70 L/h/400 L/h.

TABLE 27.9
Group 4 Compounds: RTs and Parent–Daughter Transitions (Basic Extraction and ESI+)

Native Compounds	RT (min)	Parent–Daughter (*m/z*)	Quantitation Reference
Cimetidine	6.9	253.1–159.0	Albuterol-d_3
Albuterol	9.4	240.0–148.0	Albuterol-d_3
Ranitidine	10.3	315.0–175.9	Albuterol-d_3
Metformin	11.0	131.1–60.0	Metformin-d_6
Albuterol-d_3	9.4	243.0–151.0	Cotinine-d_3
Metformin-d_6	11.0	285.1–162.0	Cotinine-d_3
Cotinine-d_3 (IS)	5.9	180.0–79.9	External standard
$^{13}C_3$-Atrazine (IS)	2.0	219.5–176.9	External standard

Notes: The labeled compounds are spiked into water to quantify the analytes. Cotinine-d_3 and $^{13}C_3$-atrazine are used as internal standards.

MS cone/desolvation: 80 L/h
MS gas rate: 400 L/h
Acquisition: MRM mode, unit resolution
LC injection volume: 15 or 5 μL

QUALITATIVE DETERMINATION AND QUANTIFICATION

The RTs of the LC peaks are compared with that in the calibration standards. The RT of the peak must fall within 15 s of its RT in the standard. The presence of a compound is confirmed from the *m/z* of parent to daughter transition as shown in Tables 27.3, 27.5, 27.7, and 27.9 for all four groups. Quantitative determination is performed by the isotope dilution method for those substances for which isotopically labeled analogs are available, and used for calibration and spiking. For all other analytes, internal standard calibration is carried out. In the isotope dilution method, compute the concentration of each compound in the sample extract using the RR from the calibration standard. The RR is determined from calibrating the native compounds with a labeled analog using the following equation:

$$\mathrm{RR} = A_\mathrm{n} \times C_\mathrm{l} / A_\mathrm{l} \times C_n$$

where
A_n is the area of the daughter *m/z* for the native compound
A_l is the area of the daughter *m/z* for the labeled compound
C_l is the concentration of the labeled compound in the calibration standard
C_n is the concentration of the native compound in the calibration standard

If the calibration is carried out by internal standard, especially for compounds for which labeled analogs are not available determine the RF from the following equation:

$$RR = A_\mathrm{n} \times C_\mathrm{is} / A_\mathrm{is} \times C_\mathrm{n}$$

where
A_n is the area of the daughter *m/z* for the native compound
A_is is the area of the daughter *m/z* for the internal standard

C_{is} is the concentration of the internal standard
C_n is the concentration of the native compound in calibration standard

If the RR or the RF for the compounds over the calibration range remain constant or fall within 20% of relative standard deviations, then the average RR or RF may be used in the calculation for quantification, otherwise use the complete calibration curve to quantify that compound. The concentration of each compound in the sample extract, C_{ex} may then be calculated from the following equations:

$$C_{ex}(\text{ng/mL}) = A_n \times C_l / A_l \times \text{RR}; \qquad \text{or} \qquad A_S \times C_{is} / A_{is} \times \text{RF}$$

The concentration of the native compound (analyte) in the aqueous or the solid sample can finally be calculated after determining its concentration in the solvent extract, C_{ex} from the following equations. The concentration of the analyte in these equations is expressed as nanogram per liter volume or nanogram per kilogram weight of sample which is ppt.

$$\text{Concentration of analyte in aqueous sample (ng/L)} = 1000 \times C_{ex} \times V_{ex} / V_s$$
$$\text{Concentration of analyte in solid sample (ng/kg)} = C_{ex} \times V_{ex} / W_s$$

where
V_{ex} is volume of extract in mL
V_s is sample volume in liters
W_s is the weight of solid sample (as dry weight) in kg

If the concentration of any compound exceeds the calibration range, dilute the sample extract appropriately to bring the concentration within the calibration range or measure a smaller portion of the sample. The dilution factor or any adjustment must be taken into account accordingly for quantification in the above equations.

QUALITY ASSURANCE/QUALITY CONTROL

Laboratories must adhere to the QA/QC protocols as described in detail in this method. Readers may refer to this U.S. EPA method for a step-by-step description. As with any analysis, the basic requirement is to obtain accurate results with high reproducibility. The acceptance criteria are defined in the method. The QA/QC requirement include initial and continued demonstration of the capability of the laboratory and the individuals performing the analysis, analysis of standards, blanks, and spiked samples, analysis of certified QC check samples periodically obtained from outside suppliers, and checking calibration prior to analysis and most important, the system performance check. The latter pertains to LC–MS/MS operating conditions and relates to the RT of calibration for the native and labeled compounds, mass calibration and optimization for mass spectrometer operation. The MS/MS scan is carried out over the mass range 20–2000 using the NaCsI calibration solution. In addition to the mass spectrometer, the performance of the LC column, the overall LC system, and the HLB SPE cartridges for the sample extractions and cleanups should be checked. The details of the procedures for these may be found in the prescribed method.

SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIME

Samples should be collected in amber glass containers. For aqueous samples, collect a total of 2 and 1 L each for the acid and base fractions, respectively. Add 80 mg sodium thiosulfate per liter sample if residual chlorine is present in the water. Ascorbic acid may also be added as a preservative for

several pharmaceuticals. Solid or semisolid samples are collected in wide mouthed jars. All samples should be stored in dark under freezing temperature. Certain compounds are susceptible to degrade rapidly. The samples should therefore be extracted within 48 h after collection. If the sample is stored in the dark in the frozen state, then the extraction time may be delayed beyond 48 h, however, it is not to exceed beyond a period of 7 days from collection. Furthermore, if the extraction cannot be performed within 48 h, then adjust the pH of the sample between 5.00 to 9.00 by adding an acid or a base, respectively. The sample after extraction should also be stored in the dark under freezing temperature. The sample extract must be analyzed within 40 days from extraction.

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28 Emerging Pollutants
Steroids and Hormones

Many steroids, hormones, and their metabolites are being detected in the environment in waters, soils, sediments, and biosolids. The identification and quantification of such pollutants at trace concentrations have therefore assumed significant importance similar to many other classes of emerging pollutants. The methods of their extractions and analyses are well discussed in the literature. The most important aspect of such methods for their applications and acceptance, and consequently for any regulatory approval therefore involve the authentic identification of these substances and the ability of such methods to detect and quantify such substances at extreme low levels to minimize any health risks from exposures. High-resolution gas chromatography–high-resolution mass spectrometry (HRGC/HRMS) should be ideal for this purpose. The instrumentations, however, are expensive and the analysis is lengthy and cumbersome. Low-resolution mass spectrometry may be used to determine the presence of the compounds for screening only if the concentrations of such compounds are relatively high. The U.S. EPA Method 1698 (Axys, 2007; U.S. EPA, 2007) describes an analytical procedure for the determination of steroids and hormones in aqueous, solids, and biosolid samples. A brief description of this method is presented below. The names and the Chemical Abstracts Service (CAS) registry numbers for the steroids and hormones determined by this method are listed in Table 28.1. Also listed are the internal standards and the labeled isotope used in this method. For the full details of this procedure in a stepwise description, readers may refer to this method.

OUTLINE OF THE PROCEDURE

Aqueous samples are extracted with methylene chloride by liquid–liquid-solvent extraction using either a separatory funnel or a continuous liquid/liquid extractor. Stable isotopically labeled analogs of the steroids and hormones are spiked into 1 L of sample prior to extraction. For solid and semisolid samples the labeled compounds are added to the sample aliquot containing 10 g dry weight of solids. The solid samples are ground and homogenized and mixed well with anhydrous sodium sulfate for drying. The dry sample then is extracted with hexane–acetone solvents mixture for 16–24 h in a Soxhlet extractor. For biosolids, the labeled compounds are spiked into the sample aliquots containing 0.25 g of dry solids, mixed with anhydrous sodium sulfate and extracted with a hexane–acetone mixture in the Soxhlet extractor.

For relatively clean samples, the cleanup of solvent extracts is not necessary. However, if the sample contains interfering substances the extract should then be cleaned up for their removal. Such cleanup can be carried over on a column containing layered basic alumina (5% deactivated, 60–325 mesh) and Florisil (60–100 mesh). Methylene chloride is exchanged to toluene–hexane (5% toluene: 95% hexane) during such column cleanup. Sulfur, if present in the sample may be removed by treating the extract with copper powder or foil. The sample extract is concentrated down to a small volume using a rotary evaporated, heating mantle or a Kuderna–Danish concentrator. During such sample concentration steps the extract must not be allowed to evaporate to dryness because any low molecular steroid and hormone present in the sample may be lost partially or fully. After this concentration, the volume of the extract is further reduced under nitrogen flow down to 0.3 mL or to an appropriate volume that may be required accordingly for the derivatization of the steroids and hormones; and to lower the detection limits of these compounds.

TABLE 28.1
Names and CAS Registry Numbers of Steroids and Hormones

Steroids/Hormones	CAS Numbers
Androstenedione	63-05-8
Androsterone	53-41-8
Campesterol	474-62-4
Cholestanol	80-97-7
Cholesterol	57-88-5
Coprostanol	360-68-9
Desmosterol	313-04-2
Desogestrel	54024-22-5
17alpha-Dihydroequilin	651-55-8
Epi-Coprostanol	516-92-7
Equilenin	517-09-0
Equilin	474-86-2
Ergosterol	57-87-4
17alpha-Estradiol	57-91-0
17alpha-Ethynyl Estradiol	57-63-6
17beta-Estradiol	50-28-2
beta-Estradiol-3-benzoate	50-50-0
Estriol	50-27-1
Estrone	53-16-7
Mestranol	72-33-3
Norethindrone	68-22-4
Norgestrel	6533-00-2
Progesterone	57-83-0
beta-Sitosterol	83-46-5
beta-Stigmasterol	83-45-4
Stigmasterol	83-48-7
Testosterone	58-22-0

Notes: The above steroids and hormones are determined by isotope dilution and internal standard by HRGC/HRMS. The labeled analogs used in this method are bisphenol A propane-d6, cholesterol-d7, diethylstilbestrol-d8, 17alpha-ethynyl estradiol-d4, 17beta-estradiol-d4, mestranol-d4, norethindrone-d6, norgestrel-d6, and progesterone-d9.

The concentrated sample extract is exchanged to pyridine to derivatize the steroids and hormones to their trimethylsilyl (TMS) ether derivatives using *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with trimethylchlorosilane (TMCS) (99% BSTFA: 1% TMCS). The calibration standard solutions should also be derivatized accordingly. The purpose of derivatization is to convert the target analytes to derivatives that are sufficiently volatile for GC/HRMS analysis. The derivatizing reagent is available commercially (e.g., Supelco and Bellefonte).

An aliquot of the extract is injected into the GC for separation of the compounds and their subsequent analysis by a high-resolution mass spectrometer interfaced to the GC. Two exact *m/z* ions are monitored for each compound for their authentic identification. Establish the operating conditions necessary to meet the retention times (RTs) for the steroids and hormones and their labeled analogs

used as internal standards. Optimize the GC conditions. The GC column and the conditions used in this method are as follow. Equivalent columns and alternate conditions may be applied if the resolution of target compounds is achieved.

SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Collect 1 L of aqueous sample for extraction and analysis. If residual chlorine is present add 80 mg sodium thiosulfate per liter of water. Store the sample in dark in a refrigerator. The sample should be extracted preferably within 48 h after collection, and if that is not possible then adjust the pH of the sample to 5.0–9.0 and extract within 7 days. Store the sample extract in dark at −10°C and analyze within 40 days of extraction. For solid and biosolid samples collect an amount that should contain at least 20 g dry solids. The storage conditions and the holding times for such solid samples are the same as that of the aqueous sample.

GC CONDITIONS

GC column, 30 m long × 0.25 mm ID × 0.25 um film thickness (Restek RTX-5 or equivalent); injector type, split/splitless; carrier gas, helium; injector temperature, 280°C; maximum temperature 325°C; oven temperature, initial 100°C, hold time 4 min, first temperature ramp 10°C/min, hold temperature 265°C, hold time 7 min, second temperature ramp 10°C/min, hold temperature 300°C, hold time 4 min, third temperature ramp 20°C/min, final temperature 310°C, hold time 3 min. (All portions of the column that connect the GC to the ion source should remain at or above the interface temperature during analysis to prevent condensation of less volatile substances.)

MS CONDITIONS

Source temperature 280°C; electron energy 35 eV; detector voltage variable; scan time 1.5 s or less (a shorter scan time gives more points and may improve peak and integration accuracy, however, a faster scan reduces channel integration time and results in a slight decrease in sensitivity. The method recommends shorter scan times below 1.5 s, an upper limit. The typical peak width at the base for these compounds under these conditions is between 9 and 24 s with a mean of 12.7 s, and with a minimum of 9 scans or data points across each peak).

Tune the mass spectrometer using perfluorokerosene (PFK) or other reference substance to meet the resolution criteria. The minimum required resolving power should be 5000 (10% valley) at *m*/*z* 280.9825 or other significant PFK fragment in the range 250–300. Because the instrument is operated in high-resolution mode, mass drift of a few ppm can have serious adverse effects on instrument performance. The mass drift correction is therefore mandatory and a lock-mass *m*/*z* is dependent on the exact *m*/*z*s monitored. The deviation between each monitored exact *m*/*z* and the theoretical *m*/*z* must be less than 5 ppm. Obtain a selected ion current profile (SICP) at two exact *m*/*z*s specified in Table 28.2 for each native and labeled compound.

CALIBRATION AND QUANTITATION

Isotope dilution is used for calibration of the native compounds for which a labeled analog is available. The relative response (RR) (labeled to native) versus concentration in the calibrated solutions is computed over the calibration range. Determine the RR of each native compound to its labeled analog using the area responses of both the primary and secondary exact *m*/*z*s for each calibration standard. The areas at the two exact *m*/*z*s for the compound are summed and divided by the summed area of the two exact *m*/*z*s for the quantitation reference. Both exact *m*/*z*s are used to reduce the effect of any interference at a single *m*/*z*. Other quantitative references and alternative procedures, however, may be applied if those give accurate results. Use the following equation for calibration:

TABLE 28.2
The RTs, Exact *m/z*, and Theoretical *m/z* Ratios for the TMS Derivatives of Steroids and Hormones

Steroids/Hormones and Labeled Standards (as TMS Derivatives)	RT (s)	Exact *m/z*		Theoretical Ratio (m_1/m_2)
		1	2	
n-Octadecanol-d37	1055	374.5401	365.5439	4.50
Pyrene-d10	1062	213.1400	214.0000	5.62
Bisphenol A propane-d6	1104	360.1894	361.1927	2.90
Androsterone	1268	347.2406	348.2440	3.44
Desogestrel	1286	353.2300	354.2334	3.21
17alpha-Estradiol	1349	416.2566	417.2600	2.67
Estrone	354	342.2015	343.2048	3.45
Androstenedione	1355	286.1933	287.1966	4.73
Equilin	1359	340.1858	341.1892	3.46
17beta-Estradiol-d4	1380	420.2817	421.2851	2.67
17beta-Estradiol	1382	416.2566	417.2600	2.67
Testosterone	1396	360.2484	361.2518	3.32
Equilenin	1425	338.1702	339.1739	3.46
Mestranol-d4	1424	371.2344	372.2378	3.21
Mestranol	1427	367.2093	368.2127	3.21
Norethindrone-d6	1434	361.2470	362.2503	3.32
Norethindrone	1438	355.2093	356.2127	3.31
17alpha-Dihydroequilin	1468	307.1913	308.1946	3.39
17alpha-Ethynyl estradiol-d4	1476	429.2583	430.2616	2.59
17alpha-Ethynyl estradiol	1478	425.2332	426.2365	2.59
Progesterone-d9	1496	323.2811	324.2844	3.09
Progesterone	1503	314.2246	315.2279	4.44
Norgestrel-d6	1535	361.2470	362.2503	3.32
Norgestrel	1540	355.2093	356.2127	3.32
Estriol	1577	504.2910	505.2944	2.17
Coprostanol	1737	370.3631	371.3664	3.18
Epicoprostanol	1745	370.3631	371.3664	3.18
Cholesterol-d6	1815	375.3913	376.3947	3.18
Cholesterol	1821	368.3474	369.3508	3.18
Cholestanol	1829	445.3865	369.3899	2.62
Desmosterol	1851	441.3552	442.3586	2.90
Ergosterol	1886	363.3447	364.3475	3.08
Campesterol	1901	382.3631	383.3664	3.08
Stigmasterol	1925	484.4100	485.4131	1.94
beta-Sitosterol	1974	486.4257	487.4290	2.41
beta-Stigmasterol	1983	488.4413	489.4447	2.41
beta-Estradiol-3-benzoate	2186	105.0340	106.0374	12.72

Notes: Calculation of accurate masses is based on most abundant fragment ion for the predominant TMS derivative. Generally, these are the M and $M + 1$ ions of the TMS ether molecular ions. There are, however, several exceptions. Use bisphenol A propane-d_6 if there is interference with *n*-octadecanol-d_{37}.

$$\text{Relative Response, RR} = \frac{(A1_n + A2_n)C_l}{(A1_l + A2_l)C_n}$$

where

$A1_n$ and $A2_n$ are the areas of the primary and secondary *m/z*s for the native compound
$A1_l$ and $A2_l$ are the areas of the primary and secondary *m/z*s for the labeled compound
C_l is the concentration of the labeled compound in the calibration standard
C_n is the concentration of the native compound in the calibration standard

Determine the linearity in RR for each native compound at each concentration. Calculate the average (mean) RR and the relative standard deviation (RSD). If the RR for any native compound is constant (less than 30% RSD) the average RR may be used for that compound. Otherwise use the complete calibration curve for that compound over the calibration range.

If labeled analogs are not available for native compounds, then use an internal standard for calibration. Determine the response factor, RF from the following equation:

$$\text{Response factor, RF} = \frac{(A1_s + A2_s)C_{is}}{(A1_{is} + A2_{is})C_s}$$

where

$A1_s$ and $A2_s$ are the areas of the primary and secondary *m/z*s for the native or labeled compound
$A1_{is}$ and $A2_{is}$ are the areas of the primary and secondary *m/z*s for the labeled injection internal standard
C_{is} is the concentration of the labeled injection internal standard
C_s is the concentration of the compound in the calibration standard

Compute the concentration of the steroid or the hormone in the extract as follow, if the quantitation method is the isotope dilution:

$$C_{ex}(\text{ng/mL}) = \frac{(A1_n + A2_n)C_l}{(A1_l + A2_l)\text{RR}}$$

where C_{ex} is the concentration of the steroid or hormone in the extract; and all other terms as defined above.

For internal standard quantitation, determine the concentration of the steroid and hormone in the extract of each native compound that does not have a labeled analog, and of each labeled compound using the response factor, RF from the following equation:

$$C_{ex}(\text{ng/mL}) = \frac{(A1_s + A2_s)C_l}{(A1_{is} + A2_{is})\text{RF}}$$

where C_{ex} is the concentration of the labeled compound in the extract and the other terms are as defined above.

The concentration of the native compound in the aqueous or the solid phase is calculated from the concentration of the compound in the extract from the following equations:

$$\text{Concentration in aqueous sample, ng/L} = \left[\frac{C_{ex}V_{ex}}{V_s}\right] \times 1000$$

$$\text{Concentration in solid sample, ng/kg} = \frac{C_{ex}V_{ex}}{W_s}$$

where

C_{ex} is the concentration of the compound in the extract
V_{ex} is the extract volume (mL)
V_s is the sample volume (L)
W_s is the sample weight (dry weight) (kg)

A known amount of a labeled steroid or hormone should be added to each sample prior to extraction. Correction for recovery for each steroid or hormone can be made accordingly as the native compound and its labeled analog exhibit similar effects upon extraction, concentration, and chromatographic response. Percent recovery is calculated as follow:

$$\text{Recovery}\,(\%) = \left\{\frac{\text{Concentration found, ng/mL}}{\text{Concentration spiked, ng/mL}}\right\} \times 100$$

QUALITY CONTROL

The laboratory performing analyses of steroids and hormones is required to operate a formal quality assurance program. The program broadly consists of initial demonstration of the laboratory's capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance (U.S. EPA, 1979). The laboratory is required to maintain records of all these from the receipts of samples and the chain of custody to system performance and calibration check, and finally determining the precision and accuracy of analysis. The full details of the procedures for quality control are described in the method. Additionally follow the instrument manual for HRGC/HRMS system performance check.

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29 Emerging Pollutants
Nanomaterials

CLASSIFICATIONS AND USES

Rapid growth in nanotechnology in recent years and its numerous applications in industries and agriculture have caused widespread emission of nanomaterials and their trace residues into the environment. Such substances may be of different types and origin: as for example, metal and metal oxide nanoparticles, such as silver, gold, ZnO_2, CeO_2, and Fe_3O_4; carbon-based materials, such as single- and multiwalled carbon nanotubes, dendrimers, and fullerenes; and quantum dots. Their origin may occur from nonengineered anthropogenic activities, such as vehicles and industrial emissions, or as manufactured materials, engineered and manipulated for their special applications, or from natural processes like volcanic eruptions. Such nanoparticles and their residues are ubiquitously found in the environment. They are susceptible to contaminate the aquatic environment, food chain, and air and therefore present the risks of causing adverse effects on human health and aquatic species. The wastewater from industrial sources, the runoff water from domestic uses, and the agricultural nanomaterials released into the soils and groundwater may all contribute to the contamination of such an aquatic environment. Likewise, the nanoparticles originating from diesel exhausts and industrial emissions can cause air contamination. The term "nanomaterials" include an array of substances of a wide variety of shape, size, and nanostructures having varying physical and chemical properties. The toxicities of such substances may also vary, depending on their physical and chemical compositions, particle size, and the routes of exposures.

The nanomaterials are composed of extremely small particles that are usually less than 100 nm size, and they are designed and fabricated to give unique functional properties to produce desired mechanical, electronic, magnetic, optical, thermal, surface, biomedical, environmental, agricultural, and nutritional characteristics for their diverse applications in multiple industrial sectors. Some of their properties and applications are highlighted in Table 29.1.

The methods for analysis of nanomaterials in environmental samples are scant. However several techniques are known for their separation and characterization in food and agricultural samples that are mostly heterogeneous consisting mixtures of a variety of nanoparticles. The samples therefore require separations prior to their characterizations.

SEPARATION, CHARACTERIZATION, AND DETECTION OF NANOPARTICLES IN FOOD AND AGRICULTURAL SAMPLES

Several techniques are known for the separation of nanomaterials. They primarily include the capillary electrophoresis (CE) and chromatographic methods. Also, flow field fractionation (FFF) techniques are often used for separations. The chromatographic methods include HPLC, ultra-performance liquid chromatography, size exclusion chromatography (SEC), and weak/strong cation or anion exchange chromatography. The techniques for separation of nanoparticles however should be based on their size, charge, polarity, hydrophobicity, and other factors. As for chromatographic separation, the selection of techniques should depend on the physical and chemical properties of nanoparticles. For example, SEC can be used if the separation is based on molecular mass. In the same way, weak or strong cation or anion exchange separation should be applied for charged nanoparticles. Reversed phase HPLC separations should be based on the hydrophobicity and polarity of nanoparticles. Colloidal suspensions and biomolecules in food and biological

TABLE 29.1
Properties and Applications of Nanomaterials

Applications/Properties	Purpose/Examples
Mechanical	Anticorrosion; resistance to wear; produce materials with stronger and lighter structures
Electronic	Capacitors for mobile phones and other small consumer devices; impart high conductivity to materials
Magnetic	Increase density storage area; improve contrast in magnetic resonance imaging (MRI) images
Optical	Anti-reflection coatings; improve refractive index surfaces; optical sensors for cancer diagnosis
Thermal	Enhance efficiency of transformer coolants; improve heat transfer from solar collectors to storage tanks
Energy	Hydrogen storage applications; electrocatalysts for fuel cells; to produce high energy and more durable batteries; in ultra-high performance solar cells
Surface	Coatings for cleaning surfaces; in specialty glasses; in surface catalytic processes
Environmental	Cleanup of oil and biodegradable contaminants from soil; water filtration processes; treatment of industrial emissions
Biomedical	Antibacterial silver coatings on dressings for wounds; sensors to detect diseases; to program drug release in drug delivery systems
Agriculture	Provide routes for delivery of pesticides to plants
Food	Packaging for food delivery; nutritional supplements; modify textures and tastes; improve colors and flavors; inhibit microbial spoilage of packaged food; used in beverages
Personal care	Sun-cream products

samples can be separated by hydrodynamic chromatography (HDC). Here the separation is based on the hydrodynamic radius of nanomaterials.

FFF is another effective method for separation of many types of nanomaterials. Two types of FFF techniques are mostly used: sedimentation and asymmetric flow. Sedimentation-FFF is used for measuring small particles in food products, such as milk and flour. Also, the method is applied to determine the particle size and elemental distributions in soil colloids. The use of such sedimentation-FFF technique combined with inductively coupled plasma (ICP)/MS has been reported in the literature for measuring particle size and the elemental distributions of nanomaterials. The asymmetric-FFF technique may also be used for characterization of nanoparticles. Its applications have been reported for characterization of Fe_3O_4/hydroxide colloids in aquatic and agricultural soil samples and humic substances. The asymmetric-FFF method combined with laser-induced breakdown of sample material is used for measuring Fe_3O_4/hydroxide colloids. For aqueous samples a detection limit of 1 mg/L can be attained.

The methods most widely used for detection of nanoparticles in food and agricultural samples are based on microscopic or spectroscopic measurements, or a combination of both. Electron microscopy is commonly applied to determine the shape, size, and other elemental properties of nanoparticles in food samples. Transmittance electron microscopy (TEM) is a suitable nanoscale imaging technique for characterization of nanoparticles of size less than 200 nm in food and agricultural samples. TEM techniques have found several applications, such as measuring shape, size, and morphology of milk-protein based nanotubes, enzyme functionalized peptide nanotubes, and serum albumin nanoparticles. Scanning electron microscopy (SEM) is employed to characterize larger particles, of size greater than 500 nm. Among its applications in food analysis are to determine the morphology of protein, polysaccharide, and liposomal nanoparticles. Other microscopy techniques include atomic force microscopy (AFM) which can determine structural irregularities in polymer materials and confocal laser microscopy to detect CeO_2 and ZnO nanoparticles aggregates in plant tissues.

Spectroscopic methods include light scattering techniques such as dynamic light scattering (DAL) (or photon correlation spectroscopy), static light scattering, phase analysis light scattering, autofluorescence, and surface plasmon resonance. These methods have been successfully utilized to measure small aggregated proteins in food samples, and for size characterization of lipid nanocapsules. The static light scattering technique can be used to measure particle size ranging from 0.05 to 2000 um. The technique has been applied to measure particle size in dairy products, skimmed milk, whole milk, and lactose crystals. Another type of spectroscopy detector is the energy dispersive x-ray (EDX) which can provide the elemental compositions of nanomaterials. In combination with TEM that can give images relating to the size, size distribution, and morphology of nanomaterials, EDX can be used to identify inorganic particles, such as silver nanoparticles. The method however is not suitable for carbon nanoparticles. Another spectroscopy method is surface-enhanced Raman spectroscopy used to detect and measure nanoparticles such as silver in food and environmental samples. The technique employs human metallothionein-based sensors as rapid screening tools to measure the size and mass of nanoparticles. Autofluorescence is another technique used for agricultural samples, such as glutaral-fixed plant samples. The presence of lignin in the cell wall of the plant tissues attributes to such autofluorescence, thus enabling the detection of magnetic nanoparticles inside the cells.

Some of the methods discussed above for characterizing nanomaterials have their own limitations. Electron microscopy studies for example can be laborious. Also, SEM and TEM instruments operate under high vacuum conditions. The samples containing water cannot be imaged, and therefore must be dehydrated fully. Also chemical fixation of samples must be done before imaging. Liquid samples and emulsions like milk or yogurt should be encapsulated first in agar or chemically fixed and then dehydrated for microscopic analysis.

ENVIRONMENTAL SAMPLES

The information available for screening, characterization, and detection of nanoparticles in environmental samples is very scant. However, the techniques employed for food and agricultural samples discussed above may also be applied to environmental samples. In general, there are three steps involved in such analysis; separation, detection, and characterization of nanoparticles. As far as the instrumentation goes, they should be one or preferably a combination of one or more of the following techniques: chromatography, spectroscopy (light scattering), and the electron microscopy. While the term characterization in reference to nanomaterials generally would refer to measuring the particle size, their size distributions, charge, surface areas, shape, and the morphology, detection should refer to their identifications, that is, chemical (elemental) compositions.

Chromatography methods also can be used to characterize nanoparticles in environmental samples. The most common chromatographic method is SEC. SEC combined with detection techniques such as, ICP-MS, voltammetry, DAL, and multiangle laser light scattering have been successfully applied for the analysis of nanogold particles. Quantum dots and single-walled carbon nanotubes can also be characterized by SEC combined with the above detection methods. Gold nanoparticles can also be separated by CE. Other chromatographic techniques include HDC and field flow fractionation (FFF) discussed above for food and agricultural samples. Characterization of fluorescent nanoparticles and colloids by HDC combined with a UV/visible detector can be achieved by these methods, although the peak resolution of HDC may be poor. FFF may be applied for the separation and analysis of metals, metal oxides, carbon black, and silica in soil suspensions and aqueous samples.

Spectroscopic methods include dynamic light scattering (DLS), laser-based scattering, x-ray scattering, Raman spectroscopy, and nuclear magnetic resonance (NMR). Application of these techniques should be based on the nature of the analysis and information required. For example, x-ray spectroscopy gives crystallographic information for characterization of nanoparticles on surfaces and coatings, whereas Raman spectroscopy provides structural information on nanoparticles.

NMR provides information on the three-dimensional (3D) structure of the sample and DLS is used to characterize particle size and their aggregation in suspensions.

Electron microscopy techniques can be applied to characterize nanomaterials in environmental samples, similar to the methods used to analyze food and agricultural samples. However, nanoparticles released into the environment are furthermore subject to be affected by oxidation, photochemical reactions, and microorganisms. Such effects can result in modifications and surface functionalization of nanomaterials, such as carbon nanotubes and fullerenes. The presence of natural organic matter contents in the sample matrix can affect especially the size and morphology of C_{60} particles. The characterization of environmental nanoparticles may therefore require special procedures.

Among the electron microscopy methods, SEM and TEM by far are the most common techniques used for characterization. TEM has been used successfully to identify carbon nanotubes and fullerenes in sediments. These methods, as well as the AFM technique can achieve resolution in subnanometer range and can therefore serve as effective tools for imaging nanoparticles to determine their size, shape, structure, aggregation, dispersion, and other properties. Another technique worth mentioning here is confocal laser scanning microscopy, which is a modification of confocal microscopy. This can detect fluorescent samples and therefore may be applied to image thick samples, such as colloids. Electron microscopy methods, as has been stated earlier, have major limitations. The most notable one is that the instruments operate in vacuum. Therefore only solid samples may be characterized. Also the technique is destructive, that is, the sample is destroyed after each analysis. The method therefore can be used only once. Also, the biological samples may require special treatment to improve contrast for imaging. Currently, SEM and other microscopic methods are being modified and combined with other techniques for imaging humic substances and natural aquatic colloids and to develop analytical methods for use in aquatic and complex biological matrices.

Optical microscopy methods have not found much application for characterizing nanomaterials, because the size of the particles is below the range of optical microscopy. However, a modified technique, known as, near-field scanning optical microscopy, that can achieve resolution between 50 and 100 nm, may be applied to image aggregates of nanoparticles. Applications of this technique in environmental analysis have not been reported.

More research is needed to develop reliable, cost effective, simple, and less cumbersome analytical techniques for separation, detection, and characterization of nanomaterials in complex environmental matrices.

30 Fluorides

Fluoride (F^-) is a halogen ion that occurs in potable water and wastewater. It may also occur in soil, sediments, hazardous waste, aerosols, and gas. While a low concentration of fluoride (below 1 ppm at a controlled level in drinking water) is beneficial for reducing dental caries, a higher content is harmful. Fluoride in water may be determined by one of the following methods:

1. Colorimetric SPADNS method
2. Colorimetric automated complexone method
3. Ion-selective electrode method
4. Ion chromatography

Methods 1 and 2 are colorimetric techniques based on the reaction between fluoride and a dye. Methods 3 and 4 are discussed in Chapters 9 and 11, respectively.

COLORIMETRIC SPADNS METHOD

In the acid medium, fluoride reacts instantaneously with zirconyl-dye lake, which is composed of zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8\ H_2O$, and sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate (SPADNS), displacing the Zr^{2+} from the dye lake to form a colorless complex anion, ZrF_6^{2-} and the dye. As a result, the color of the solution lightens as the concentration of F^- increases.

Chlorine, carbonates, bicarbonates, and hydroxides are common interferences. The former is removed by adding a drop of 1% solution of sodium arsenite ($NaAsO_2$). If the sample is basic, neutralize it with HNO_3. The sample may be diluted to reduce the interference effect.

Procedure

Prepare a standard calibration curve using fluoride standards from 0 to 1.5 mg F^-/L. A 50 mL volume of standard solutions is treated with 10 mL of zirconyl-acid–SPADN reagent mixture. The intensity of the color is measured either by a spectrophotometer at 570 nm or a filter photometer equipped with a greenish yellow filter having maximum transmittance from 550 to 580 nm. The absorbance reading of the standards and the sample are noted after setting the photometer to zero absorbance with the reference solution (zirconyl-acid–SPADN mixture). The concentration of fluoride is determined from the calibration standard curve, taking dilution of the sample, if any, into consideration.

Zirconyl-acid–SPADN reagent is made by combining equal volumes of SPADNS with zirconyl-acid reagent. The former is prepared by dissolving 1 g of SPADNS in 500 mL distilled water. The latter is made by dissolving 0.14 g zirconyl chloride octahydrate in 50 mL of distilled water followed by addition of 350 mL conc. HCl and dilution to 500 mL.

AUTOMATED COLORIMETRIC METHOD

The analysis is performed using a continuous flow analytical instrument such as Technicon Autoanalyzer or equivalent. The sample is distilled and the distillate, free of interference, is reacted with alizarin fluorine blue [$C_{14}H_7O_4 \cdot CH_2N(CH_2 \cdot COOH)_2$]–lanthanum reagent to form a blue complex. The absorbance is measured at 620 nm. Standard fluoride solutions are prepared in the range from 0.1 to 2.0 mg F^-/L using the stock fluoride solution.

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31 Haloacetic Acids

Haloacetic acids are an important class of disinfection by-products that have been linked to bladder, kidney, and rectal cancers in human. These substances are produced along with a variety of other halogenated organic compounds during chlorination of natural waters. Because of their potential health effects and widespread occurrences, these substances are regulated in drinking water in the United States. The term haloacetic acids refer to the halogenated compounds of acetic acid, CH_3COOH, in which the H atom(s) of the methyl group ($-CH_3$) are replaced by one or more Cl or Br atom(s). Some common haloacetic acids found in chlorinated water include monochloroacetic acid (MCA), $ClCH_2COOH$; monobromoacetic acid (MBA), $BrCH_2COOH$; dichloroacetic acid (DCA), $Cl_2CHCOOH$; bromochloroacetic acid (BCA), $BrClCHCOOH$; trichloroacetic acid (TCA), Cl_3CCOOH; dibromoacetic acid (DBA), $Br_2CHCOOH$; bromodichloro acetic acid (BDCA), $BrCl_2CCOOH$; dibromochloroacetic acid (DBCA), $Br_2ClCCOOH$; and tribromoacetic acid (TBA), Br_3CCOOH.

Haloacetic acids in aqueous samples can be measured by the U.S. EPA Methods 551.1, 552.1, and 552.2 and by the APHA/AWWA/WEF Method 6251B. These methods do not differ much from each other in their analytical procedures. These methods are based on partitioning haloacetic acids from acidified waters into a suitable immiscible organic solvent, followed by derivatizing these compounds into their methyl esters and then separating the ester derivatives on a capillary GC column and detecting the acids using an ECD. A typical procedure is outlined below.

A 50 mL volume of sample is acidified to a pH below 0.5 with sulfuric acid. It is then extracted using either 3 mL methyl *tert*-butyl ether (MTBE) or 5 mL pentane. The haloacetic acids are converted into their methyl esters by treating the MTBE solution with acidic methanol and heating for 1 or 2 min. Anhydrous sodium sulfate is then added into this solution mixture for the removal of excess methanol and product water. The solution is then neutralized to pH 7 with saturated solution of sodium bicarbonate. The aqueous layer is discarded and a 2 μL extract solution is withdrawn and injected onto the GC-ECD for analysis. Concentrations are measured using standard calibration procedure with an internal standard. The presence of analytes is confirmed on an alternate column. In an alternative procedure (U.S. EPA Method 552.1), a 100 mL sample is adjusted to pH 5 and extracted using a preconditioned miniature anion exchange column. The haloacetic acids are eluted with small amounts of acidic methanol. They are then esterified directly after adding a small volume of MTBE as a cosolvent. The ester derivatives partition into the MTBE phase and analyzed with a capillary GC equipped with an ECD.

ALTERNATIVE METHODS

Several methods have been reported in the literature for measuring haloacetic acids in water. Most of these methods are modifications of the U.S. EPA methods. A majority of these methods are based on liquid–liquid microextraction using MTBE, followed by esterification with acidic methanol and analyzing the methyl esters of the haloacetic acids by GC-ECD or GC/MS. One such procedure (Nikolaou et al., 2002) is outlined below.

To 30 mL sample, 5 μL solution of a surrogate standard (60 mg/L 2-bromopropionic acid in MTBE) (Surrogate 1) is added. This is followed by addition of 3 mL conc. H_2SO_4 (to pH below 0.5), 6 g anhydrous Na_2SO_4, 3 g $CuSO_4 \cdot 5H_2O$ and 2 mL MTBE. The vials are sealed, shaken for 2 min, and then allowed to stand for 5 min. A 900-μL volume of this extract solution is then transferred into a 14 mL vial containing 2 mL of 10% solution of H_2SO_4 in methanol. Into this solution, 1 μL of a second surrogate standard (60 mg/L 2,3-dibromopropionic acid in MTBE) (Surrogate 2) is added.

The vials are placed for 1 h in a water bath at 50°C after which they are cooled to 4°C for 10 min. This is followed by adding 5 mL aqueous solution of either 5% $CuSO_4 \cdot 5H_2O$ or 10% aqueous solution made from anhydrous Na_2SO_4. The vials are shaken gently for 2 min and allowed to stand for 5 min. An aliquot volume 300 μL of this final extract is transferred into a 2 mL vial from which 1 μL quantity is injected onto the GC for ECD or mass spectrometric (MS) measurement. The GC and the MS conditions in the above reference are given below as an example. Any equivalent column and alternate conditions that give proper resolution and meet the QC criteria may be employed.

Column: fused silica capillary DB-1 column, 30 m × 0.32 mm id × 0.25 um film thickness (GC-ECD); fused silica capillary HP-VOC, 60 m × 0.32 mm × 1.8 um (GC/MS); carrier gas flow: 1.6 mL/min (GC), 1.3 mL/min (MS), makeup gas flow 46 mL/min (GC); split ratio 1:25; injector temp 175°C; detector temp 300°C (ECD), 280°C (MS); oven temp 35°C (9 min), 1°C/min to 40°C (3 min), 6°C/min to 220°C (10 min), the final oven temp for MS analysis 150°C; solvent delay 14 min (MS).

Xie (2001) has described a GC/MS method to analyze nine haloacetic acids and dalapon in water. This method too is based on microextraction and acidic methanol derivatization similar to the other methods discussed above. The compounds, however, are measured by GC/MS under the SIM mode. The method as the author claimed offered shorter run time, fewer interfering peaks, cleaner baselines, and higher sensitivity for MCAA in comparison to the GC-ECD method. In addition, the method performance is comparable to that of the U.S. EPA Method 552.2. Under the electron impact ionization, the most abundant ion characterizing all the nine haloacetic acids is *m/z* 59, $[COOCH_3]^+$, followed by *m/z* 49, $[CH_2Cl^{35}]^+$. The haloacetic acids as their methyl esters may be identified from their RTs in the SIM chromatograms and quantified from the abundance of mass ion 59.

Scott and Alaee (1998) have developed an *in situ* derivatization technique to measure haloacetic acids in environmental waters. Their method involves the reduction of the sample volume first to 50 mL after which the haloacetic acids in the sample concentrate are derivatized with 2,4-difluoroaniline in ethyl acetate using dicyclohexylcarboimide as catalyst. The anilide derivatives produced are measured by GC/MS in the SIM mode. While the mono-substituted acids are quantified from their characteristic mass ion at *m/z* 129 the di- and the trisubstituted acids are quantified from their mass ion 156. Trifluoroacetic acid anilide is quantified from its most abundant mass ion at *m/z* 225.

Wang and Wong (2005) have described a method to measure DCAs and TCAs in drinking water by acidic methanol esterification and headspace GC using ECD. The authors reported that the esterification with acidic methanol carried out in water was more efficient than that with diazomethane in organic solvent. The detection limits were 3 and 0.5 μg/L for DCAs and TCAs, respectively. The use of *tert*-amyl methyl ether, a higher boiling point solvent, instead of MTBE improved the methylation of brominated trihaloacetic acids (Domino et al., 2004).

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32 Halogenated Hydrocarbons

Halogenated hydrocarbons or halocarbons are halogen-substituted hydrocarbons. These substances contain carbon, hydrogen, and halogen atoms in the molecules. They are widely used as solvents, dry cleaning and degreasing agents, refrigerants, fire extinguishers, surgical anesthetics, lubricants, and intermediates in the manufacture of dyes, artificial resins, plasticizers, and pharmaceuticals. Because of their wide applications, these compounds are found in the environment in trace quantities and constitute an important class of regulated pollutants. Most halogenated hydrocarbons are liquids at ambient temperature and pressure. Some low-molecular weight compounds such as methyl chloride or vinyl chloride are gases. Compounds of higher molecular weight, such as iodoform, are solids at ambient conditions. The U.S. EPA has listed several halogenated hydrocarbons as priority pollutants and their methods of analysis are documented (U.S. EPA 1984–1992; Methods 601, 612, 624, 625, 501, 502, 503, 524, 8240, and 8260). In this chapter, halogenated hydrocarbons are defined as halogen-substituted compounds of alkane, alkene, cycloalkane, and aromatic classes, but polychlorinated biphenyls and chlorinated pesticides like BHC isomers are excluded. Their methods of analyses are based on their physical properties, such as volatility, boiling point, and water solubility. Halogenated hydrocarbons may be analyzed using any one of the following methodologies:

1. Purge and trap concentration (or thermal desorption) from the aqueous matrices (aqueous samples or aqueous extracts of nonaqueous samples or methanol/acetone extract of nonaqueous samples spiked into reagent-grade water), separation of the analytes on a suitable GC column and their determination using a halogen-specific detector or a mass spectrometer.
2. Liquid–liquid extraction or liquid–solid extraction for aqueous samples (and Soxhlet extraction or sonication for nonaqueous samples), followed by sample concentration, cleanup, and determination by GC or GC/MS. Direct injection, waste dilution, or other extraction techniques, depending on the sample matrices, may be used.

In general, the purge and trap technique is applied to analyze substances that have boiling points below 200°C and are insoluble or slightly soluble in water. Heating of the purging chamber may be required for compounds that are more soluble. Soils, sediments, and solid wastes should be extracted with methanol or acetone, and an aliquot of the extract is spiked into reagent-grade water in the purging vessel for purge and trap extraction. Alternatively, an aliquot of the aqueous extract of the solid matrix may be subjected to purge and trap concentration. In either case, highly volatile compounds are susceptible to mechanical loss during such two-step extraction processes. Such highly volatile analytes in solid matrices may be determined by thermal desorption of a weighed aliquot of the sample, as is, under an inert gas purge.

The purge and trap system consists of a purging device, a trap, and a desorber. Such systems are commercially available from several sources. The purging device is a glass vessel that can accept samples with a water column at least 5 cm deep. The headspace above the sample should be less than 15 L if the sample volume is 5 mL. The base of the sample chamber should have a glass frit so that the purge gas passes through the water column, producing bubbles with a diameter of 3 mm at the origin.

The trap should consist of 2,6-diphenylene oxide polymer (Tenax GC grade), silica gel, and coconut charcoal, each constituting a one-third portion. A methyl silicone packing at the inlet can extend the life of the trap. Tenax alone may be used if only compounds boiling above 35°C are to be analyzed. A silica gel trap is required for highly volatile compounds, while charcoal effectively adsorbs dichlorodifluoromethane and related compounds.

The desorber is a heating device capable of rapidly heating the trap to 180°C. Trap failure may be noted from poor bromoform sensitivity or may be characterized from a pressure drop over 3 psi across the trap during purging. The Tenax section of the trap should not be heated over 200°C.

The U.S. EPA's analytical procedures mention an 11 min purge with nitrogen or helium at a flow rate of 40 mL/min; and 4 min desorption at 180°C, backflushing the trap with an inert gas at 20–60 mL/min. A 5 mL sample volume is recommended for purging. A larger volume of sample may be required to obtain a lower detection level. Other conditions may be used if precision and accuracy of the analysis are met.

A halogen-specific detector, such as an electrolytic conductivity detector (ELCD) or a microcoulometric detector, determines the analytes separated on the GC column. An ECD, FID, quadrupole mass selective detector, or ion trap detector (ITD) may also be used. A PID may also be used to determine unsaturated halogenated hydrocarbons such as chlorobenzene or trichloroethylene. Among the detectors, ELCD, PID, and ECD give a lower level of detection than FID or MS. The detector operating conditions for the ELCD are listed below:

- ELCD: Tracor Hall model 700-A detector or equivalent.
- Reactor tube: Nickel 1/16 in. outer diameter.
- Reactor temperature: 810°C.
- Reactor base temperature: 250°C.
- Electrolyte: 100% *n*-propyl alcohol.
- Electrolyte flow rate: 0.8 mL/min.
- Reaction gas: Hydrogen at 40 mL/min.
- Carrier gas: Helium at 40 mL/min.
- GC column: A capillary column of intermediate polarity can give adequate resolution of isomers as well as unsaturated compounds. Many such columns are commercially available. These include 105 m long × 0.53 mm ID, Rtx-502.2; 60 m long × 0.75 mm ID, VOCOL; 60 m long × 0.53 mm ID, DB-62 or equivalent. Other capillary columns include 95% dimethyl-5% diphenyl polysiloxane coated columns, such as DB-5, SPB-5, Rtx-5, AT-5, or equivalent. These columns are also suitable for the separation of a number of nonhalogenated organic compounds of intermediate polarity.

Table 32.1 lists some commonly used volatile halogenated hydrocarbons. Most of these are U.S. EPA listed pollutants. The term "volatile" indicates that these substances may be extracted by the purge and trap technique. This also includes a few compounds of relatively moderate boiling range, responding adequately to the purge and trap method. The characteristic masses for the GC/MS determination are also presented in the table.

SOLVENT EXTRACTION

Low volatile, high molecular weight halogenated compounds can be extracted with hexane or isooctane and determined by GC-ECD. Methylene chloride may be used for extraction if the analysis is done by GC/MS. The purge and trap efficiency will be poor for such compounds, especially those boiling over 200°C. Soils, sediments, and solid wastes may be extracted with methylene chloride by sonication or Soxhlet extraction. Interferences from acidic compounds, such as chlorophenol, may be removed by acid–base partitioning cleanup. The extract is then concentrated and analyzed by GC/MS or exchanged to hexane and analyzed by GC-ECD.

Nonpurge and trap extraction, such as liquid–liquid microextraction, can be used for many volatile compounds with boiling points well below 200°C. Similarly, the purge and trap method can be used for compounds boiling well over 200°C, especially when the purging chamber is heated.

Table 32.2 presents some of the halogenated hydrocarbons that can be effectively extracted out from aqueous and nonaqueous matrices by liquid–liquid or other nonpurge and trap extraction.

TABLE 32.1
Purgeable Volatile Halogenated Hydrocarbons and Their Characteristic Masses

CAS No.	Compounds Determined by ELCD/PID	Characteristic Masses for GC/MS Identification[a]	
		Primary Ion (*m/z*)	Secondary Ions (*m/z*)
[107-05-1]	Allyl chloride[b]	76	41, 39, 78
[100-44-7]	Benzyl chloride[b]	91	126, 65, 128
[108-86-1]	Bromobenzene[b]	156	77, 158
[74-97-5]	Bromochloromethane	128	49, 130
[75-27-4]	Bromodichloromethane	83	85, 127
[460-00-4]	4-Bromofluorobenzene	95	174, 176
[75-25-2]	Bromoform	173	175, 254
[56-23-5]	Carbon tetrachloride	117	119
[108-90-7]	Chlorobenzene[b]	112	77, 114
[126-99-8]	2-Chloro-1,3-butadiene[b]	56	49
[124-48-1]	Chlorodibromomethane	129	208, 206, 127
[67-66-3]	Chloroform	83	85
[544-10-5]	1-Chlorohexane	84	49, 51
[563-47-3]	3-Chloro-2-methyl propene[b]	55	39, 90
[126-99-8]	Chloroprene	53	88, 90, 51
[107-05-1]	3-Chloropropene[b]		–
[95-49-8]	2-Chlorotoluene	91	126
[106-43-4]	4-Chlorotoluene	91	126
[96-12-8]	1,2-Dibromo-3-chloropropane[c]	75	155, 157
[106-93-4]	1,2-Dibromoethane	107	109, 188
[74-95-3]	Dibromomethane	93	95, 174
[95-50-1]	1,2-Dichlorobenzene	146	111, 148
[106-47-7]	1,4-Dichlorobenzene	146	111, 148
[1476-11-5]	*cis*-1,4-Dichloro-2-butene	75	53, 77, 124, 89
[110-57-6]	*trans*-1,4-Dichloro-2-butene[c]	53	75, 88
[75-71-8]	Dichlorodifluoromethane	85	87
[75-34-3]	1,1-Dichloroethane	63	65, 83
[107-06-2]	1,2-Dichloroethane	62	98
[75-35-4]	1,1-Dichloroethene[b]	96	61, 63
[156-59-2]	*cis*-1,2-Dichloroethene[b]	96	61, 98
[156-60-5]	*trans*-1,2-Dichloroethene[b]	96	61, 98
[78-87-5]	1,2-Dichloropropane	63	112
[142-28-9]	1,3-Dichloropropane	76	78
[594-20-7]	2,2-Dichloropropane	77	97
[563-58-6]	1,1-Dichloropropene[b]	75	110, 77
[542-75-6]	1,3-Dichloropropene[b]	75	77, 110
[10061-01-5]	*cis*-1,3-Dichloropropene[b]	75	77, 39
[10061-02-6]	*trans*-1,3-Dichloropropene[b]	75	77, 39
[540-36-3]	1,4-Difluorobenzene[b]	114	–
[74-96-4]	Ethyl bromide	108	110
[75-00-3]	Ethyl chloride	64	66
[106-93-4]	Ethylene dibromide	107	109, 188
[462-06-6]	Fluorobenzene[b]	96	77
[87-68-3]	Hexachlorobutadiene[b]	225	223, 227
[67-72-1]	Hexachloroethane	201	166, 199, 203
[74-83-9]	Methyl bromide	94	96
[74-87-3]	Methyl chloride	50	52
[75-09-2]	Methylene chloride	84	86, 49
[74-88-4]	Methyl iodide	142	127, 141

(*Continued*)

TABLE 32.1 (*Continued*)
Purgeable Volatile Halogenated Hydrocarbons and Their Characteristic Masses

CAS No.	Compounds Determined by ELCD/PID	Characteristic Masses for GC/MS Identification[a]	
		Primary Ion (*m/z*)	Secondary Ions (*m/z*)
[76-01-7]	Pentachloroethane	167	130, 132
[363-72-4]	Pentafluorobenzene[b]	168	165, 169
[630-20-6]	1,1,1,2-Tetrachloroethane	131	133, 199
[79-34-5]	1,1,2,2-Tetrachloroethane	83	131, 85
[127-18-4]	Tetrachloroethylene[b]	164	129, 131, 166
[87-61-6]	1,2,3-Trichlorobenzene[b]	180	182, 145
[120-82-1]	1,2,4-Trichlorobenzene[b]	180	182, 145
[71-55-6]	1,1,1-Trichloroethane	97	99, 61
[79-00-5]	1,1,2-Trichloroethane	83	97, 85
[79-01-6]	Trichloroethylene[b]	95	97, 130, 132
[75-69-4]	Trichlorofluoromethane	101	103, 151, 153
[96-18-4]	1,2,3-Trichloropropane	75	77
[75-01-4]	Vinyl chloride[b]	62	64

[a] Electron-impact ionization mode.
[b] Compounds that also show PID response.
[c] Poor purging efficiency.

TABLE 32.2
Some Solvent Extractable Halogenated Hydrocarbon Pollutants and Their Characteristic Masses

CAS No.	Compound Determined by GC-ECD and GC/MS	Characteristic Ions for GC/MS Identification	
		Primary (*m/z*)	Secondary (*m/z*)
[100-39-0]	Benzyl bromide	91	170, 172
[100-44-7]	Benzyl chloride	91	126, 65, 128
[108-86-1]	Bromobenzene	156	77, 158
[90-13-1]	1-Chloronaphthalene	162	127, 164
[95-49-8]	2-Chlorotoluene	91	126
[106-43-4]	4-Chlorotoluene	91	126
[96-12-8]	1,2-Dibromo-3-chloropropane	75	155,157
[95-50-1]	1,2-Dichlorobenzene	146	148, 111
[541-73-1]	1,3-Dichlorobenzene	146	148, 111
[106-46-7]	1,4-Dichlorobenzene	146	148, 111
[106-93-4]	Ethylene dibromide	107	109, 188
[118-74-1]	Hexachlorobenzene	284	142, 249
[87-68-3]	Hexachlorobutadiene	225	223, 227
[77-47-4]	Hexachlorocyclopentadiene	237	235, 272
[67-72-1]	Hexachloroethane	117	201, 199
[70-30-4]	Hexachlorophene	196	198, 209, 406
[1888-71-7]	Hexachloropropene	213	211, 215, 117
[608-93-5]	Pentachlorobenzene	250	252, 108, 248, 215
[95-94-3]	1,2,4,5-Tetrachlorobenzene	216	214, 179, 108, 143
[120-82-1]	1,2,4-Trichlorobenzene	180	182, 145

Such compounds include di-, tri-, tetra-, penta-, and hexahalo-substituents aromatics and cyclohexanes, and haloderivatives of alkanes with a carbon number greater than 6. Characteristic mass ions for GC/MS identification are also presented for some of these listed compounds.

SAMPLE COLLECTION AND PRESERVATION

Samples should be collected in a glass container without headspace and refrigerated. If volatile compounds are to be analyzed by the purge and trap method, the analysis must be done within 14 days of sampling. If substances of low volatility are to be determined following solvent extraction, the extraction should be performed within 14 days and analysis within 30 days from extraction. U.S. EPA methods, however, mention a 7-day holding time for solvent extraction (for semivolatile organic pollutants that include some halogenated hydrocarbons), and a 45-day holding time for the analysis after extraction.

If residual chlorine is present, add sodium thiosulfate (~100 mg/L) for its removal. Ascorbic acid may also be added to reduce residual chlorine. The latter is preferred if the analysis includes gaseous halocarbons.

The use of plastic containers should be avoided because phthalate impurities can interfere in ECD determination.

INTERNAL STANDARDS/SURROGATES AND TUNING COMPOUNDS

Several compounds, including many deuterated and fluoro derivatives have been used in the published literature. These include fluorobenzene, pentafluorobenzene, 1,2-dichlorobenzene-d_4, 1-chloro-2-fluorobenzene, 1,4-difluorobenzene, 1,2-dichloroethane-d_4, 1,4-dichlorobutane, and 2-bromo-1-chloropropane. The U.S. EPA has set the tuning criteria for bromofluorobenzene and decafluorotriphenylphosphine as tuning compounds for volatile and semivolatile organic compounds (see Chapter 4).

AIR ANALYSIS

The NIOSH, ASTM, and U.S. EPA methods can determine common halogenated hydrocarbons in air. The NIOSH methods, in general, are based on adsorption of compounds in the air over a suitable adsorbent, desorption of the adsorbed analytes into a desorbing solvent, and, subsequently, their determination by GC using a suitable detector. A known volume of air is drawn through a cartridge containing coconut shell charcoal. The adsorbed compounds are desorbed into carbon disulfide, propanol, benzene, toluene, hexane, or methylene chloride. An aliquot of the solvent extract is then injected onto the GC column. FID is the most commonly used detector. Other detectors, such as ECD, ELCD, or PID have been used, however, in the method development of certain compounds. NIOSH method numbers and the analytical techniques are presented in Table 32.3.

Sampling of halogenated hydrocarbons in ambient air as per U.S. EPA methods (TO-1, TO-2, TO-3, and TO-14) may be performed using one of the three general techniques: (1) adsorption, (2) cryogenic cooling, and (3) canister sampling. In the adsorption method of air sampling, a measured volume of air is drawn through a cartridge containing an adsorbent such as Tenax (GC grade) or carbon molecular sieve. The former is effective in adsorbing substances that have boiling points in the range of 80–200°C. The carbon molecular sieve, on the other hand, is suitable for highly volatile halocarbons having boiling points in the range of −15°C to +120°C. Unlike the NIOSH methods that require desorption of analytes with a solvent, these methods (TO-1 and TO-2) are based on the thermal desorption technique. The cartridge is placed in a heated chamber and purged with an inert gas. The desorbed compounds are transferred onto the front of a GC column held at low temperature (–70°C) or to a specially designed cryogenic trap from which they are flash evaporated onto the precooled GC column.

TABLE 32.3
NIOSH Methods for Air Analysis for Halogenated Hydrocarbons

Compounds	NIOSH Method	Desorbing Solvent	GC Detector
Benzyl chloride, bromoform, carbon tetrachloride, chlorobenzene, chlorobromomethane, *o*-and ρ-dichlorobenzene, 1,1-dichloroethane, 1,2-dichloroethane, ethylene dichloride, hexachloroethane, tetrachloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,2,3-trichloropropane	1003	CS_2	FID
Allyl chloride	1000	Benzene	FID
Bromotrifluoromethane	1017	CH_2Cl_2	FID
Dibromodifluoromethane	1012	Propanol	FID
Dichlorodifluoromethane, 1,2-dichlorotetrafluoroethane	1018	CH_2Cl_2	FID
Dichlorofluoromethane	2516	CS_2	FID
1,2-dichloropropane	1013	Acetone/cyclohexane (15:85)	ELCD
Ethyl bromide	1011	2-Propanol	FID
Ethyl chloride	2519	CS_2	FID
Ethylene dibromide	1008	Benzene/methanol (99:1)	ECD
Hexachlor-1,3-cyclopentadiene	2518		ECD
Methyl bromide	2520	CS_2	FID
Methyl chloride	1001	CH_2Cl_2	FID
Methyl iodide	1014	Toluene	FID
Pentachloroethane	2517	Hexane	ECD
1,1,2,2-Tetrabromoethane	2003	Tetrahydrofuran	FID
1,1,2,2-Tetrachloroethane	1019	CS_2	FID
1,1,2,2-Tetrachloro-2,2-difluoroethane, 1,1,2,2-tetrachloro-1,2-difluoroethane	1016	CS_2	FID
Trichloroethylene	1022/3701	CS_2	FID/PID[a]
Trichlorofluoromethane	1006	CS_2	FID
1,1,2-Trichloro-1,2,2-trifluoroethane	1020	CS_2	FID
Vinyl bromide	1009	Ethanol	FID
Vinyl chloride	1007	CS_2	FID
Vinylidene chloride	1015	CS_2	FID

Note: FID, flame ionization detector; ECD, electron capture detector; ELD, electrolytic conductivity detector; GC, gas chromatograph; PID, photoionization detector.

[a] Air directly injected into a portable GC, equipped with a PID.

Many volatile, nonpolar organics that have boiling points in the range of –10°C to +200°C, which include several halogenated hydrocarbons, can be collected in a trap placed in liquid argon or oxygen. After the sampling (drawing a measured volume of air) through the trap, the liquid cryogen is removed. The contents of the trap are swept with a carrier gas under heating to a precooled GC column. Alternatively, air may be collected in a passivated canister (SUMMA Model) initially evacuated at subatmospheric pressure or under pressure using a pump. The collected air in the canister is transferred and concentrated in a cryogenically cooled trap from which it is transported onto a GC column by the techniques described above.

The compounds are separated on the GC column, temperature programmed, and determined by an ECD, FID, or MS. Although these methods were developed for a limited number of specific compounds, the same methods may be applied to related compounds. Selection of the methods should

TABLE 32.4
U.S. EPA Methods for the Air Analysis of Halogenated Hydrocarbons

Compounds	U.S. EPA Methods
Allyl chloride	TO-2, TO-3
Benzyl chloride	TO-1, TO-3, TO-14
Carbon tetrachloride	TO-1, TO-2, TO-3, TO-14
Chlorobenzene	TO-1, TO-3, TO-14
Chloroprene	TO-1, TO-3
1,2-Dibromoethane	TO-14
1,2-Dichlorobenzene	TO-14
1,3-Dichlorobenzene	TO-14
1,4-Dichlorobenzene	TO-1, TO-14
1,1-Dichloroethane	TO-14
1,2-Dichloroethane	TO-14
1,2-Dichloroethylene	TO-14
1,2-Dichloropropane	TO-14
1,3-Dichloropropane	TO-14
Ethyl chloride	TO-14
Freon-11, -12, -113, and -114	TO-14
Hexachlorobutadiene	TO-14
Methyl chloride	TO-14
Methylene chloride	TO-2, TO-3, TO-14
Tetrachloroethylene	TO-1, TO-2, TO-3, TO-14
1,2,3-Trichlorobenzene	TO-10, TO-14
1,2,4-Trichlorobenzene	TO-14
1,1,1-Trichloroethane	TO-1, TO-2, TO-3, TO-14
1,1,2-Trichloroethane	TO-14
Vinyl chloride	TO-2, TO-3, TO-14
Vinyl trichloride	TO-14
Vinylidine chloride	TO-2, TO-3, TO-14

be based on the boiling points of the halogenated hydrocarbons. Table 32.4 presents the U.S. EPA's method numbers for air analysis of halogenated hydrocarbons. Analysis of compounds not listed in Table 32.4, however, may be performed by similar procedures, based on their boiling points.

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33 Hardness

Hardness of a water sample is a measure of its capacity to precipitate soap. The presence of calcium and magnesium ions in water essentially contributes to its hardness. Other polyvalent ions, such as aluminum, also cause hardness. Their effect, however, is minimal, because these polyvalent ions occur in water often in complex forms and not as free ions. As a result, they cannot precipitate soap. Although calcium is not the only cation causing hardness, for the sake of convenience, hardness is expressed as mg $CaCO_3$/L. Similarly, anions other than carbonate, such as bicarbonate, also cause hardness in water. To distinguish the contributions of such anions from carbonates, hardness is sometimes termed as "carbonate hardness" and "noncarbonate hardness." This can be determined from alkalinity. The relationship is as follows.

When the total hardness measured in the sample is numerically greater than the sum of both carbonate alkalinity and bicarbonate alkalinity, then

$$\text{Carbonate hardness} = \text{carbonate alkalinity} + \text{bicarbonate alkalinity}$$

and

$$\text{Noncarbonate hardness} = \text{total hardness} - \text{carbonate hardness}$$

or

$$\text{Total hardness} - (\text{carbonate alkalinity} + \text{bicarbonate alkalinity})$$

When total hardness is equal to or less than the sum of carbonate and bicarbonate alkalinity, all hardness is noncarbonate hardness only and there is no carbonate hardness.

Hardness can be measured by either (1) calculation from the concentration of calcium and magnesium ions in the sample or (2) EDTA titration.

HARDNESS DETERMINATIONS

Calculation

Analyze the metals, calcium, and magnesium in the sample using atomic absorption spectrophotometry or any other suitable technique and determine their concentrations.

Compute hardness as mg equivalent $CaCO_3$/L, as follows:

$$\text{Hardness, mg equivalent } CaCO_3/L = 2.497 \times (\text{conc. of Ca, mg/L}) + 4.118 \times (\text{conc. of Mg, mg/L})$$

The factors 2.497 and 4.118 are obtained by dividing the formula weight of $CaCO_3$ (100.09) by atomic weights of Ca (40.08) and Mg (24.30), respectively.

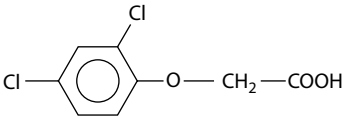
Titration

Hardness can be measured precisely by EDTA titration. The principle of this titrimetric method is discussed extensively under Chapter 6.

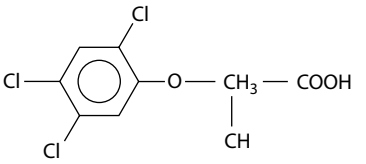
EDTA and its sodium salt readily react with calcium, magnesium, and certain other metal cations to form soluble chelates. Certain dyes, such as Calmagite or Eriochrome-Black T used as color indicators, also react with these metal ions, especially, Ca^{2+} and Mg^{2+} forming colored complexes. Thus, Ca and Mg ions combine with the indicator molecules, producing a wine red color at the pH 10. Thus, the sample pH is adjusted to 10 by using a buffer and made wine red before the titration by adding the indicator solution to it. The addition of titrant forms more stable Ca-EDTA and Mg-EDTA complexes, displacing Ca^{2+} and Mg^{2+} from their respective chelates with the indicator. Thus, the end point of titration signifies the completion of chelation of all Ca and Mg ions in the sample with the titrant EDTA. This results in the dissociation of all metal–indicator complex molecules. The wine red color turns blue. To enhance the sharpness of the end point, a small amount of magnesium salt of EDTA is added to the buffer.

34 Herbicides
Chlorophenoxy Acid

Chlorophenoxy acids are one of the most important classes of chlorinated herbicides. In these compounds, chlorosubstituted benzene rings are attached to lower carboxylic acids via an oxygen atom, as shown in the following structures.



(2,4-Dichlorophenoxy) acetic acid or 2,4-D



(2,4,5-Trichlorophenoxy)-2-propionic acid or silvex

Some of the common chlorophenoxy acid herbicides are listed in Table 34.1.

The method of analysis primarily involves four basic steps: (1) extraction of herbicides from the sample into an organic solvent, (2) hydrolysis of the extract, (3) esterification, and (4) gas chromatographic (GC) determination of the herbicide esters formed.

ANALYSIS

Sample Extraction

Aqueous samples are extracted with diethyl ether while soils, sediments, and solid wastes are extracted with acetone and diethyl ether. Prior to extraction, the sample is acidified with HCl to a pH below 2. Such acidification is necessary due to the fact that in nature or in the environmental matrix, herbicides may occur as acids, salts, or esters. Acidification converts all these forms into chlorophenoxy acids.

Aqueous sample after acidification is extracted thrice with ether. The herbicide acids are now in the ether phase (top layer). The aqueous phase is discarded.

In the case of solids, the sample (~50 g) is moistened with water and is acidified with HCl under stirring. The content is then mixed with 25 mL acetone and is shaken for several minutes. To this, about 100 mL diethyl ether is added and the mixture shaken further for several minutes. The extract is decanted and collected. The above extraction steps are repeated twice more. The extracts are combined together and the pH is checked. HCl is added, if required, to maintain the pH below 2. Allow the layers to separate. The aqueous layer is discarded.

2,4-Dichlorophenylacetic acid is recommended as a surrogate standard in the U.S. EPA Method 8151.

TABLE 34.1
Some Common Chlorophenoxy Acid Herbicides

CAS No.	Common Name	Chemical Name
[94-75-7]	2,4-D	(2,4-dichlorophenoxy) acetic acid
[93-76-5]	2,4,5-T	(2,4,5-trichlorophenoxy) acetic acid
[93-72-1]	Silvex	(2,4,5-trichlorophenoxy) propionic acid
[94-82-6]	2,4-DB	4-(2,4-dichlorophenoxy) butyric acid
[94-74-6]	MCPA	(4-chloro-2-methylphenoxy) acetic acid
[120-36-5]	Dichlorprop	2-(2,4-dichlorophenoxy) propionic acid
[1918-00-9]	Dicamba	3,6-dichloro-2-methoxybenzoic acid

Hydrolysis

Herbicide acids extracted into the ether are now hydrolyzed with KOH and water. Such a hydrolysis step is important for removing most extraneous organic materials from the sample. Add 20–30 mL organic free reagent grade water and a few milliliters of 37% KOH solution into the ether extract and evaporate the ether on a water bath. Use boiling chips in all heating operations. Hydrolysis converts the chlorophenoxy acids into their potassium salts that are soluble in water. The aqueous solution of the potassium salts of herbicides are shaken repeatedly with ether in the separatory funnel. Ether wash removes most extraneous organic matter. The top ether layer is discarded. The whole purpose of alkaline hydrolysis as mentioned is to remove the organic interference and to clean up the sample.

The potassium salts of the herbicides are then converted back to their acids by treatment with H_2SO_4. The aqueous solution is acidified with cold 1:3 H_2SO_4 to pH below 2. The chlorophenoxy acids regenerated are then extracted into ether in a separatory funnel by repeat extractions. The aqueous phase is discarded in order to achieve complete esterification of herbicide acids. The ether extract containing herbicides must be completely free from moisture even at the trace level. Therefore, add acidified anhydrous Na_2SO_4 to the extract in excess amount ($\sim$10 g). The mixture is shaken well and is allowed to stand for at least a few hours.

After drying (removal of water), the extract is quantitatively transferred into a Kuderna–Danish flask equipped with a concentrator tube and a Snyder column for sample concentration. The apparatus is placed in a water bath and ether is evaporated out. Use boiling chips in all heating operations. The volume of the extract is concentrated down to 1–2 mL.

Esterification

Chlorophenoxy acids after being extracted out from the sample matrix, separated from organic interferences, and concentrated down into a small volume of ether are now converted into their methyl esters. Such esterification of herbicides is essential for their determination by GC. While chlorophenoxy acids themselves show poor response, their ester derivatives produce sharp peaks with good resolution.

Esterification may be performed by using either diazomethane (CH_2N_2) or boron trifluoride–methanol (BF_3–CH_3OH). Other esterifying reagents include BCl_3–methanol, BCl_3–butanol, and pentafluorobenzyl bromide. The latter two produce butyl and pentafluorobenzyl derivatives, respectively. All U.S. EPA methods mention the use of diazomethane for esterification. An advantage of diazomethane is that the reaction goes to completion and that many chlorinated herbicides (containing carboxylic groups), other than the chlorophenoxy types, esterify efficiently. The presence of water mars the reaction. A major disadvantage of using diazomethane, however, is that

the compound is a carcinogen and can explode under the following conditions: heating over 90°C, grinding or stirring its solution, or contact with alkali metals.

Diazomethane reacts with chlorophenoxy acid herbicides at room temperature to form the methyl esters. It is generated by combining 2 mL ether, 1 mL carbitol, 1–2 mL 37% KOH, and 0.2 g Diazald. Diazomethane formed is purged with nitrogen at a flow of 10 mL/min, and bubbled through the ether extract of the herbicides for about 10 min. On the other hand, a Diazaldkit may be used to produce diazomethane. About 2 mL of the diazomethane solution obtained from the generator kit is allowed to stand with the herbicide extract for 10 min with occasional swirling. The solvent is evaporated at room temperature. Residue formed is dissolved in hexane for GC analysis. Any unreacted diazomethane is destroyed by adding 0.2 g silicic acid and allowing it to stand until there is no more evolution of nitrogen gas.

Methanol can be used instead of diazomethane for the esterification of herbicides. The reaction is catalyzed by BF_3. To 1 mL of herbicide extract, add an equal amount of toluene or benzene. This is followed by 1 mL of BF_3–methanol. The solution is heated in a water bath for a few minutes. Ether evaporates out. Addition of a few milliliters of water partitions unreacted methanol and BF_3 into the aqueous phase, while the methyl esters of herbicides remain in the upper layer of benzene or toluene. The extraction steps discussed above are summarized in the following schematic diagram (Figure 34.1).

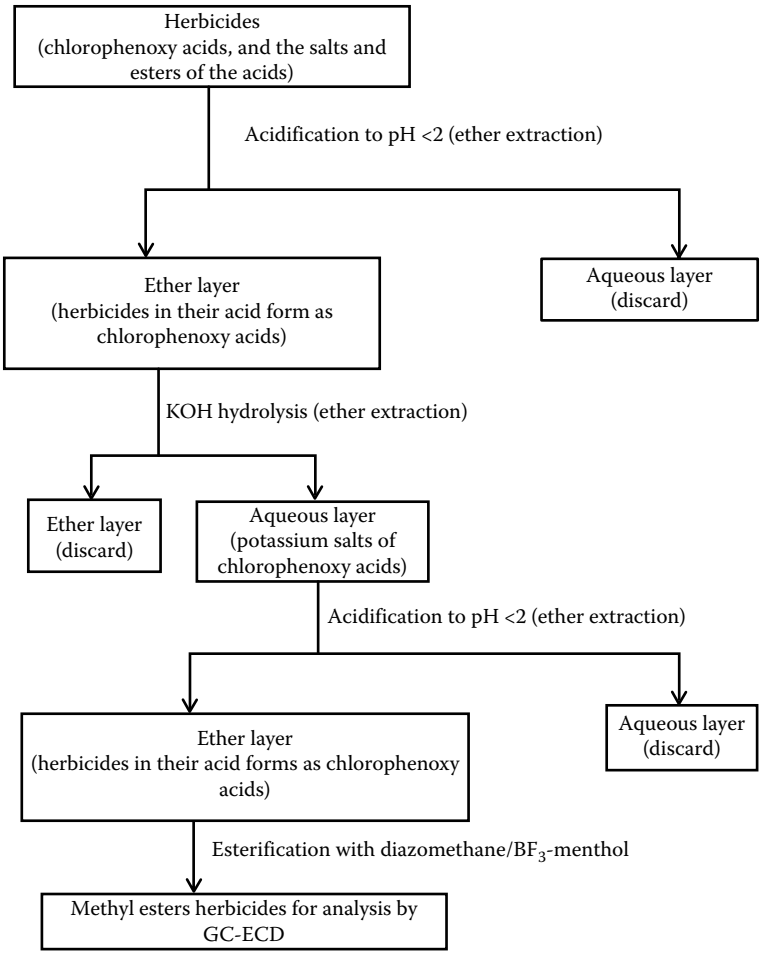


FIGURE 34.1 Schematic diagram of the extraction steps in herbicides.

Gas Chromatographic Analysis

GC using an ECD analyzes the methyl esters of herbicides. A microcoulometric detector or ELCD may alternatively be used. GC/MS, if available, should be employed to confirm the presence of analytes. Other instrumental techniques include GC-FID and HPLC. The latter can measure the acids for which esterification is not required.

Several packed and capillary columns have been reported in the U.S. EPA methods, research literature, and manufacturers' product catalogs. Some common columns are described below.

Packed column: 1.8 m × 4 mm ID glass packed with either (1) 1.5% SP 2250/1.95% SP-2401 on Supelcoport (100/120 mesh); (2) 5% OV-210 on Gas Chrom Q (100/120 mesh); or (3) 1.5% OV-17/1.95% QF-1. Efficient separation can also be achieved on a 2 mm ID column. Use 5% argon-95% methane carrier gas at flow rate of 60–70 mL/min when using a 4 mm ID column, while for a 2 mm ID column the carrier-gas flow rate should be 20–30 mL/min. An oven temperature isothermal between 160°C and 190°C should be suitable. Under the above conditions of temperature and carrier-gas flow rate, most chlorophenoxy acid methyl esters elute within 10 min on a 4 mm ID packed column.

The fused silica capillary columns give better separation than packed columns. Columns having inside diameters of 0.25, 0.32, and 0.53 mm and film thickness between 0.25 and 1 μm have found use in the analysis of herbicides. The stationary phase is generally made out of phenyl silicone, methyl silicone, and cyanopropyl phenyl silicone in varying compositions. Some common columns are DB-5, DB-1701, DB-608, SPB-5, SPB-608, SPB-1701, Rtx-5, AT-1701, HP-608, BP-608, or equivalent. Use helium as carrier gas; flow rate 30 cm/s on narrow bore columns with 0.25 or 0.32 mm ID and 7 mL/min for mega-bore 0.53 ID columns.

The methyl esters can be also determined by GC-FID. Using a 30 m × 0.32 mm ID × 0.25 μm (film thickness) capillary column, such as DB-1701 or equivalent, the compounds can be adequately separated and detected by FID. The recommended carrier gas (helium) flow rate is 35 cm/s, while that of the makeup gas (nitrogen) is 30 cm/min. All of the listed herbicides may be analyzed within 25 min. The oven temperature is programmed between 50°C and 260°C, while the detector and injector temperatures should be 300°C and 250°C, respectively. The herbicides may alternatively be converted into their trimethylsilyl esters and analyzed by GC-FID under the same conditions. FID, however, gives a lower response as compared with ECD. The detection level ranges from 50 to 100 mg. For quantitation, either the external standard or the internal standard method may be applied. Any chlorinated compound stable under the above analytical conditions, which produces a sharp peak in the same RT range without coeluting with any analyte, may be used as an internal standard for the GC-ECD analysis. The U.S. EPA Method 8151 refers the use of 4,4′-dibromooctafluorobiphenyl and 1,4-dichlorobenzene as internal standards. The quantitation results are expressed as acid equivalent of esters. If pure chlorophenoxy acid neat compounds are esterified and used for calibration, the results would determine the actual concentrations of herbicides in the sample. Alternatively, if required, the herbicide acids can be stoichiometrically calculated as follows from the concentration of their methyl esters determined in the analysis:

$$\text{Conc. of herbicide acid} = \text{Conc. of methyl esters} \times \frac{\text{Molecular wt. of acid}}{\text{Molecular wt. of ester}}$$

The molecular weights of herbicide acids are presented under individual compounds listed alphabetically in Section III. To determine the molecular weights of the respective methyl esters, add 14 to the molecular weights of the corresponding chlorophenoxy acids.

AIR ANALYSIS

Analysis for 2,4-D and 2,4,5-T in the air may be performed using NIOSH Method 5001. Other chlorophenoxy acid herbicides such as 2,4,5-TP, 2,4-DB, and MCPA can be analyzed in the

same general way. The method involves HPLC determination of herbicides in the form of acids or salts but not their esters.

Between 20 and 200 L, air at a flow rate of 1–3 L/min is passed through a glass fiber filter. The herbicides and their salts, deposited on the filter, are desorbed with methanol, and the chlorophenoxy acid anions are determined by HPLC using an UV detector at 284–289 nm. The LC eluent is a mixture of $NaClO_4$–$Na_2B_4O_7$ at 0.001 M concentration. Other eluent composition and UV detector wavelength may be used. A stainless steel column 50 cm × 2 mm ID, packed with Zipax Sax™ or equivalent may be used at ambient temperature and 1000 psi.

As mentioned, the HPLC-UV method determines the herbicides as acids and salts only. If the esters are also to be measured, the analytes should be desorbed with an acetone–water mixture, acidified, extracted with ether, and analyzed by GC-ECD following hydrolysis and esterification as described earlier in this chapter.

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35 Herbicides
Glyphosate

Glyphosate (GLYPH) [1071-83-6] is used as a herbicide in lawns, gardens, and agriculture. The toxicity of this compound, however, unlike many other herbicides, is of low order. This herbicide is also known as glyphosphate and roundup. Its chemical names are *N*-(phosphonomethyl) glycine and isopropylamine GLYPH, its molecular formula is $C_3H_8NO_5P$, and its chemical structure is $O{=}P(OH)_2CH_2NHCH_2C(=O)OH$. It is susceptible to break down to aminomethylphosphonic acid (AMPA). Both GLYPH and its metabolite AMPA are found at trace levels in many environmental waters. They can be measured precisely by both HPLC and GC/MS. The latter, however, is the most confirmative technique. When using HPLC, its presence in the sample must be confirmed by using two columns. A brief outline of a few selected analytical methods is given below.

WATER ANALYSIS

HPLC Method

A detailed procedure is presented in the "Standard Methods for the Examination of Waters and Wastewaters" (APHA, AWWA, and WEF, 1998). The GLYPH and AMPA in the aqueous sample are separated on an anion or cation exchange column. The separated compounds are then subjected to postcolumn fluorescence derivatization reactions. A fluorescent detector with an excitation wavelength 230 nm (deuterium) or 340 nm (quartz halogen or xenon) and emission wavelength between 420 and 455 nm measure the fluorescent derivatives of these compounds formed. The reaction steps are summarized below.

GLYPH (a secondary amine) is oxidized using calcium hypochlorite solution into glycine, a primary amine. The latter on treatment with *o*-phthalaldehyde and mercaptoethanol forms an isoindole derivative. AMPA, a primary amine, is directly converted into isoindole using the same *o*-phthalaldehyde–mercaptoethanol mixture.

The HPLC system consists of an analytical column packed with either an anion exchange resin or a cation exchange resin, a postcolumn reactor, and a fluorescence detector (a filter or grating fluorimeter). The oxidation reagent solution is made by dissolving 0.5 g $Ca(OCl)_2$ in 500 mL reagent-grade water with rapid stirring for an hour using a magnetic stirrer. A 10 mL volume of this stock solution is added into an aqueous solution containing 1.74 g KH_2PO_4, 11.6 g NaCl, and 0.4 g NaOH. The mixture is diluted to a final volume of 1 L. The cation exchange mobile phase is prepared by dissolving 0.68 g KH_2PO_4 in 1 L methanol–water (4:96) and adjusting the pH to 2.1 with H_3PO_4. The fluorogenic labeling reagent is prepared by slowly dissolving 100 g boric acid and 72 g KOH in about 700 mL over a period of 1–2 h and then adding 5 mL of *o*-phthalaldehyde solution (0.8 g in 5 mL methanol) and 2 mL mercaptoethanol into this mixture. The HPLC calibration standard solutions are made from the primary and secondary stock standard solutions by serial dilution at the appropriate range of concentrations in 0.001 M disodium EDTA salt solution (0.37 g disodium ethylenediaminetetraacetate dihydrate in 1 L water).

Sampling and Storage

Aqueous samples are collected in polypropylene bottles. Sodium thiosulfate solution should be added into the sample to destroy any residual chlorine present that may react with the GLYPH. Samples should be stored below 4°C away from light and analyzed within 2 weeks.

Detection Limit

The minimum detection limit by the above HPLC method has been reported to be 25 μg/L by direct injection and can be reached to 0.5 μg/L following concentration steps. Such concentrations if desired can be carried out in a rotary evaporator after acidifying the sample, evaporating to dryness under a stream of nitrogen and then dissolving the residue in 2.9 mL mobile phase and 0.1 mL 0.03 M EDTA solution and adjusting the pH to 2.

MISCELLANEOUS METHODS FOR ANALYSIS OF GLYPH RESIDUES IN WATER, SOIL, SLUDGE, FRUIT, AND VEGETABLE EXTRACTS

Several methods are documented in the research literature for the analysis of GLYPH, AMPA, and glufosinate residues in different matrices including water, soil, sludge, fruits, and vegetables. De Llasera et al. (2005) have described a method of quantitative extraction of GLYPH and AMPA residues from tomato fruits followed by their derivatization with 9-fluorenylmethylchloroformate (FMOC) and detection by HPLC fluorescence. A dispersion column packed with 0.5 g sample blended into 1 g NH_2-silica was used in this method. AMPA was eluted first with deionized water. GLYPH was then eluted with 0.005 M solution of NaH_2PO_4. Cleanup of both the aqueous fractions were made by ion exchange chromatography on anion exchange silica. The authors have reported detection limits of 0.05 μg/g for GLYPH and 0.03 μg/g for AMPA, respectively.

Ibanez et al. (2005) have described a method for analyzing GLYPH, glufosinate, and AMPA in water and soil samples. The compounds were derivatized with 9-FMOC in borate buffer and detected by LC coupled to electrospray tandem MS (LC–ESI–MS/MS). Aqueous samples were injected directly onto an online solid phase extraction (SPE) cartridge interfaced to the LC column and a mass spectrometer. The SPE cartridges were used essentially for preconcentration of the samples. The soil samples were extracted with KOH solutions and the extracts were then injected directly onto the LC column without any preconcentration on the SPE cartridge. All the three compounds in the aqueous samples could be quantified at the concentrations of 50 ng/L and in soil samples at 0.05 mg/kg. The recoveries of GLYPH from the groundwater samples in this method, however, were low. Such recovery could be increased to 98% when the samples were acidified with HCl to a pH 1, neutralized, and then derivatized immediately with FMOC reagent before their analysis by LC–MS/MS (Ibanez et al., 2006).

Ghanem et al. (2007) have described a method for the determination of GLYPH and AMPA in sewage sludge. Their method involved an alkaline extraction from the sludge followed by purification on a strong anion exchange resin. The resin also served as a solid support for the derivatization reaction. The analytes bound onto the resin by ionic interaction were derivatized with FMOC in less than 10 min on this solid support. The derivatives formed were eluted with NaCl solution of water/acetonitrile mixture (70/30 by volume). After appropriate dilution and pH adjustment, the derivatized sample extract was concentrated on a solid phase cartridge (Oasis HLB cartridge). The concentrated extracts were then analyzed by LC–ESI–MS/MS. The limits of detection for GLYPH and AMPA by this method have been reported to be 20 and 30 ppb, respectively.

Immunosensors have been successfully applied for measuring GLYPH in water and soil (Clegg et al., 1999; Gonzalez-Martinez et al., 2005; Lee et al., 2002). Gonzalez-Martinez et al. (2005) have described a fully automated immunosensor for measuring GLYPH in water and soil. Their method involves carrying out an online derivatization reaction of GLYPH prior to assay and uses a selective anti-GLYPH serum, a GLYPH peroxidase enzyme-tracer, and a fluorescent detector. The assay time is stated to be 25 min and the detection limit 0.02 μg/L. Such a sensor can be reused over 500 analytical cycles. The procedure described by Lee et al. (2002) uses succinic anhydride to derivatize GLYPH mimicking epitotic attachment of GLYPH to horseradish peroxidase hapten. Such immunoassay measurement proceeds through an effective derivatization process and the method exhibits a high degree of precision and accuracy comparable to that obtained in a nonimmunoassay

method such as the one involving HPLC/MS detection after derivatizing the analyte online on the SPE cartridge with 9-fluorenylmethyl chloroformate.

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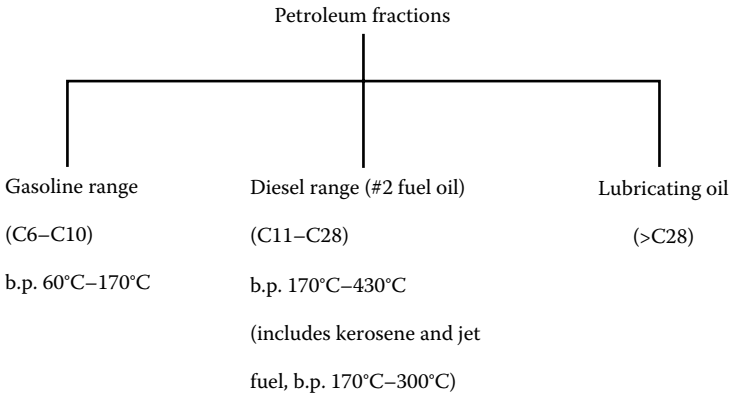
36 Hydrocarbons

Hydrocarbons are organic compounds containing only C and H atoms in the molecules. The broad class of organic compounds includes alkanes, alkenes, alkynes, cycloalkanes (naphthenes), and aromatics. Hydrocarbons occurring in nature are natural gases (mainly methane), crude oil (which is a complex mixture of alkanes, aromatics, and naphthenes of wide-ranging carbon numbers), and coals and coal tars, many of which consist of fused polyaromatic rings. Cracking or distillation of crude oil produces various petroleum fractions for their commercial applications. These fractions, as shown below, are distinguished by their carbon numbers, boiling range, and commercial uses and they include gasoline, kerosene, jet fuel, diesel oil, lubricating oil, and wax.



These petroleum products may be found in the environment from trace to significant amounts in groundwater, industrial wastewater and sludges, soils, sediments, and solid wastes.

ANALYSIS

TPHs and the various petroleum and coal tar fractions in aqueous and nonaqueous samples can be determined by methods based on IR spectrometry and GC techniques as summarized below.

- TPHs—freon extraction followed by IR spectroscopy or extraction with methanol or methylene chloride and determination by GC-FID.
- Gasoline—purge and trap extraction and determination by GC using an FID, or a PID and FID in series, or a mass spectrometer (MS).
- Diesel range organics (including kerosene and jet fuel)—extraction with methylene chloride or an appropriate solvent and analysis by GC-FID.
- PAHs (a coal-tar distillate fraction)—solvent extraction and determination by HPLC, GC-FID, or GC/MS. Enzyme immunoassay testing may be applied for semiquantitative determination.

Total Petroleum Hydrocarbons

Analysis for TPHs in aqueous and nonaqueous samples involves extraction of sample aliquots with a fluorocarbon solvent, such as freon, followed by the determination of the hydrocarbons in the extract by IR spectroscopy measuring absorbance at the wavelength 2930 cm^{-1}. Aqueous samples are repeatedly extracted with freon in a separatory funnel. The freon extract (bottom layer) is

separated and dried with anhydrous Na_2SO_4 before the IR analysis. Nonaqueous samples are mixed with anhydrous Na_2SO_4 and extracted with freon in a Soxhlet apparatus for 3–4 h. Dark, dirty, or colored extract is treated with silica gel to remove the color before IR measurement. SFE or sonication may be performed instead of Soxhlet extraction. The efficiency of extraction, however, must be established by performing duplicate analysis and determining the percent spike recovery. A calibration curve should be prepared for quantitation (plotting absorbance against concentration of calibration standards), which may be made from chlorobenzene, isooctane, and tetradecane or from any other petroleum fraction.

GC analysis involves two separate analyses: (1) for gasoline range organics by purge and trap extraction followed by FID or PID-FID determination (see Chapter 4 for details of purge and trap method) and (2) for diesel range organics by methylene chloride extraction and FID detection. The results of both analyses are summed to calculate the TPH. If gasoline range organics are not determined separately by the purge and trap method, methylene chloride at room temperature can extract most components of gasoline except the highly volatile ones, and the result for TPHs can be fairly determined by GC-FID.

Gasoline Range Organics

Gasoline is a mixture of C5–C10 hydrocarbons containing alkanes, aromatics, and their alkyl substituents, boiling in the range of 60–170°C. While the major alkane components of gasoline include pentane, hexane, methylhexane, isooctane, and their isomers, the aromatic components primarily constitute benzene, toluene, ethylbenzene, xylenes, and other alkyl benzenes. The GC chromatograms of gasoline range organics should generally constitute the peaks eluting between 2-methylpentane and 1,2,4-trimethylbenzene.

Aqueous samples can be analyzed by purge and trap extraction, followed by GC determination using FID or PID-FID connected in series. PID or FID can determine the aromatic fractions.

An inert gas is bubbled through the sample. The volatile hydrocarbons are transferred into the vapor phase and trapped over a sorbent bed containing 2,6-diphenylene oxide polymer (Tenax GC). A methyl silicone (3% OV-1 on Chromosorb-W, 60/80 mesh) packing protects the trapping material from contamination. Other adsorbents such as Carbopack B and Carbosieve S III may also be used. If pentane and other low boiling hydrocarbons need to be detected, the sorbent trap should be filled with activated charcoal, silica gel, and Tenax, respectively, in equal amounts.

The gasoline components are desorbed from the trap by heating the trap at 180°C. If Carbopack B and Carbosieve S III are used as adsorbents, the desorption and baking temperatures of the trap should be increased to 250°C and 300°C, respectively. The desorbed components are separated on a capillary column and determined by FID, PID-FID in series, or MSD.

The capillary column should be able to resolve 2-methylpentane from the methanol solvent front (when gasoline in soil is to be determined) and ethylbenzene from *m*/*p*-xylene. A 30 m × 0.53 mm ID × 1.0 μm film fused silica capillary column, such as DB-5, SPB-5, AT-5, or equivalent should give adequate separation. Columns with other dimensions can also be used. A longer column, for example, Rtx 502.2 (105 m × 0.53 mm × 0.3 μm) gives excellent resolution, but with a longer analysis time.

Diesel Range Organics

Diesel or fuel oil is a mixture of alkanes in the range C10–C28 boiling between approximately 170°C and 430°C.

The method of analysis involves extraction of 1 L of aqueous sample (liquid–liquid extraction) or 25 g of soil (sonication, Soxhlet extraction, or SFE) or an appropriate amount of the sample with methylene chloride. The extract is dried, concentrated to a volume of 1 mL, and injected into a capillary GC column for separation and detection by FID. For quantitation, the area or

height response of all peaks eluting between C10 and C28 are summed and compared against the chromatographic response of the same peaks in a #2 fuel or diesel oil standard. A 10-component *n*-alkanes mixture containing even numbered alkanes ranging between 10 and 28 C atoms has been recommended as an alternative calibration standard. These alkanes occur in all types of diesel oils, and each compound constitutes, approximately, a 1% total mass of diesel fuel, that is, 1 g of diesel fuel contains about 10 mg each of any of the above alkanes. Therefore, when using the latter as a calibration standard, the result must be multiplied appropriately by 100.

EXAMPLE 36.1

A 25 g soil sample was extracted with methylene chloride and the extract was concentrated to a final volume of 2 mL. A 10-component alkane mixture at a concentration of each component at 50 μg/mL was used in quantitation performed by the external standard method. 1 μL of the extract and the standard were injected onto the column for analysis. Determine the concentration of diesel range organics in the sample from the following data:

Sum of the area response for the 10-component standard = 370,000
Sum of the area response for the same 10 components in the sample extract = 290,000
Thus, the concentration of these alkanes in the extract

$$= \frac{290{,}000}{370{,}000} \times 50\ \mu g/mL = 39.2\ \mu g/mL \text{ of each component}$$

This is approximately equivalent to 39.2 μg/mL × 100 + 3920 μg/mL of total diesel fuel in the sample extract. Therefore, the concentration of diesel fuel in the sample is

$$= \frac{3920\ \mu g}{1\,mL} \times \frac{2\ mL}{25\ g} \times \frac{1000\ g}{1\,kg} = 313{,}600\ \mu g/kg \text{ or } 313.6\ mg/kg$$

Unlike gasoline, the chromatographic response for all alkanes in diesel, especially, the ones greater than C22, are not similar. However, a fairly accurate result may be obtained by comparing the area or height response of the alkanes below C24 (between C10 and C22) in both the standard and the sample extract.

An internal standard may be added onto the extract and the quantitation may be performed by the IS method. The surrogates recommended are *o*-terphenyl and 5A-Androstane.

For quantitation using an IS, determine the RF as follows:

$$RF = \frac{\text{Total area (or height) or 10 diesel components in the sample extract}}{\text{Area (or height) of IS}} \times \frac{\text{Concentration of IS (mg/L)}}{\text{Concentration of 10 component standard (mg/L)}}$$

The RF should be determined using standards at various concentrations, and an average RF value should be used in the calculation. Both the external standard and internal standard calibration methods for GC analysis are fully discussed in Chapter 3.

Thus, the concentration of 10 components in the sample is

$$\frac{A_s \times C_{is} \times V_t \times D}{A_{is} \times RF \times V_s}$$

where

A_s and A_{is} are the area (or height) response for the analyte and IS, respectively
V_t is the mL of the final extract

V_s is the volume of sample extracted in L (or kg)
D is the dilution factor ($D = 1$, if the extract is not diluted)

As mentioned earlier, if a 10-component alkane mixture is used as the standard, the result obtained from IS or the extraction standard calibration must be multiplied by 100 because each alkane constitutes about 1% mass of diesel fuel. If a #2 fuel oil or a diesel oil standard is used instead of a 10-component alkane mixture, and when all the major peaks in the sample extract and standards are taken into consideration, then the result must not be multiplied by 100.

37 Hydrocarbons, Polynuclear Aromatic

PAHs are aromatic compounds that contain two or more benzene rings that are fused together. These substances may be analyzed by HPLC, GC, GC/MS, and enzyme immunoassay techniques. The latter is a rapid screening method that may be applied for a qualitative or semiquantitative determination. Test kits are commercially available for such screening. The U.S. EPA (1995) has specified a method (Draft Method 4035) that detects a range of PAHs to different degrees and measures the composite of individual responses to determine the total PAHs in the sample.

The U.S. EPA has listed 16 PAHs as priority pollutants in wastewater and 24 PAH in the category of soils, sediments, hazardous wastes, and groundwater. Some common PAH compounds including the ones listed by the U.S. EPA as priority pollutants are presented in Table 37.1. All these analytes, as well as any other compound that has a polyaromatic ring, may be analyzed by similar methods. The analytical steps include extraction of the sample with methylene chloride or an appropriate solvent, concentration of the solvent extract into a small volume, cleanup of the extract using silica gel (for dirty samples), and determination of PAH by HPLC, GC, or GC/MS. The HPLC method is superior to packed column GC analysis that suffers from a coelution problem.

The latter does not adequately resolve the following four pairs of compounds:

- Anthracene and phenathrene
- Chrysene and benzo(*a*)anthracene
- Benzo(*b*)fluoranthene and benzo(*k*)fluoranthene
- Dibenzo(*a*,*h*)anthracene and indeno(1,2,3-*cd*)pyrene

These and some other coeluting substances may, however, be separated on a 30 or 60 m fused silica capillary column with 0.32 or 0.25 mm ID. On the other hand, the HPLC analysis is faster than the capillary GC determination. The presence of a compound detected must be confirmed on an alternate column or by GC/MS. A major problem with GC/MS identification is, however, that some of the compounds produce the same characteristic masses, as shown below:

1. Phenanthrene and anthracene
2. Chrysene and benzo(*a*)anthracene
3. Benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, and benzo(*a*)pyrene
4. Fluoranthene and pyrene
5. Benzo(*g*,*h*,*i*)perylene and indeno(1,2,3-*cd*)pyrene

Benzo(*a*)pyrene and the compounds in the pairs 4 and 5 may, however, be distinguished from their retention times.

HPLC COLUMNS AND CONDITIONS

- Reverse phase column: HC-ODS Sil-X 25 cm × 2.6 mm ID and 5 μm particle diameter or Vydac 201 TP with similar dimensions.
- Detector: UV (at 254 nm) or fluorescence.
- Mobile phase: 40%–100% acetonitrile in water.

TABLE 37.1
Common PAHs

CAS No.	Compounds
[83-32-9]	Acenaphthene
[208-96-8]	Acenaphthylene
[120-12-7]	Anthracene
[53-96-3]	2-Acetylaminofluorene
[56-55-3]	Benz(*a*)anthracene
[205-99-2]	Benzo(*b*)fluoranthene
[207-08-9]	Benzo(*k*)fluoranthene
[191-24-2]	Benzo(*g*,*h*,*i*)perylene
[50-32-8]	Benzo(*a*)pyrene
[192-97-2]	Benzo(*e*)pyrene
[90-13-1]	1-Chloronaphthalene
[91-58-7]	2-Chloronaphthalene
[218-01-9]	Chrysene
[191-07-1]	Coronene[a]
[224-42-0]	Dibenz(*a*,*j*)acridine
[53-70-3]	Dibenz(*a*,*h*)anthracene
[132-64-9]	Dibenzofuran
[192-65-4]	Dibenzo(*a*,*e*)pyrene
[57-97-6]	7,12-Dimethylbenz(*a*)anthracene
[206-44-0]	Fluoranthene
[86-73-7]	Fluorene
[193-39-5]	Indeno(1,2,3-*cd*)pyrene
[56-49-5]	3-Methylcholanthrene
[91-57-6]	2-Methylnaphthalene
[91-20-3]	Naphthalene
[602-87-9]	5-Nitroacenaphthene
[198-55-0]	Perylene[a]
[85-01-8]	Phenanthrene
[213-46-7]	Picene[a]
[129-00-0]	Pyrene

[a] Not listed under the U.S. EPA's list of priority pollutants.

GC COLUMNS AND CONDITIONS

- GC packed column: 1.8 m × 2 mm ID packed with 3% OV-17 on Chromosorb W-AW-DCMS (100/120 mesh) or equivalent.
- Detector-FID: 100°C for 4 min, 8°C/min to 280°C carrier gas N_2 flow rate 40 mL/min. Other column and conditions may be used.
- GC capillary column: 30 m × 0.25 mm ID × 0.25 μm film fused silica capillary column such as PTE-5, DB-5, or equivalent.

MS CONDITIONS

- Scanning range: 35–500 amu.
- Scanning time: 1 s/scan using 70 V (nominal) electron energy in the electron-impact ionization mode.

The characteristic mass ions for the PAH are presented in Table 37.2.

TABLE 37.2
Characteristic Ions for Polynuclear Aromatic Hydrocarbons

Compounds	Primary Ions	Secondary Ions
Acenaphthene	154	152, 153
Acenaphthylene	152	151, 153
Anthracene	178	176, 179
2-Acetylaminofluorene	181	152, 180, 223
Benz(*a*)anthracene	228	226, 229
Benzo(*b*)fluoranthene	252	125, 253
Benzo(*k*)fluoranthene	252	125, 253
Benzo(*g*,*h*,*i*)perylene	276	138, 277
Benzo(*a*)pyrene	252	125, 253
1-Chloronaphthalene	162	127, 164
2-Chloronaphthalene	162	127, 164
Chrysene	228	226, 229
Dibenz(*a*,*j*)acridine	279	250, 277, 280
Dibenz(*a*,*h*)anthracene	278	139, 279
Dibenzofuran	168	139
1,2:4,5-Dibenzopyrene	302	150, 151
7,12-Dimethylbenz(*a*)anthracene	256	120, 239, 241
Fluoranthene	202	101, 203
Fluorene	166	165, 167
Indeno(1,2,3-*cd*)pyrene	276	138, 227
3-Methylcholanthrene	268	126, 134, 252
2-Methylnapthalene	142	141
Naphthalene	128	127, 129
5-Nitroacenaphthene	199	141, 152, 169
Phenanthrene	178	176, 179
Pyrene	202	200, 203
Surrogates/IS		
Acenaphthene-d_{10}	164	162, 160
Chrysene-d_{12}	240	120, 236
Naphthalene-d_8	136	68
Perylene-d_{12}	264	260, 265
Phenanthrene-d_{10}	188	94, 80

SAMPLE EXTRACTION AND CLEANUP

Aqueous samples are extracted with methylene chloride by liquid–liquid extraction in a separatory funnel or a liquid–liquid extractor. The extract is concentrated to 1 mL for GC analysis. If HPLC analysis were to be performed, methylene chloride should be exchanged to acetonitrile by evaporating the solvent extract with a few mL of acetonitrile and adjusting the final volume to 1 mL.

If interferences are suspected to be present or if the sample is dirty, a silica gel cleanup should be performed.

Aqueous samples may alternatively be extracted by SPE using reversed phase C-18 stationary phase column, such as Supelclean ENVI-18. The column must be conditioned with toluene–methanol (10:1), methanol, and deionized water, respectively, prior to sample addition. The PAH analytes are eluted with toluene–methanol (10:1) mixture.

Soils, sediments, and solid wastes are mixed with anhydrous Na_2SO_4 and extracted with methylene chloride by sonication or Soxhlet extraction. SFE may be performed using CO_2. A typical set of conditions is given below:

- Solvent: CO_2
- Temperature and pressure: 100°C at 4000 psi
- Flow rate: 600 mL/min (for 15 min)
- Restrictor: Fused silica, 30 cm × 50 μm ID
- Collection: 4 mL, methylene chloride

AIR ANALYSIS

PAHs have very low vapor pressure at room temperature. These substances, however, may deposit on the dusts in the air. PAH may be produced during pyrolysis of organic materials. These compounds can contaminate the air near coke ovens, as well as during loading and unloading of pencil pitch.

The analysis of the particle-bound PAH involves collection of the PAH bound to dust particles on 0.8 μm glass fiber or silver membrane filters, desorption of the PAH from the particles into a suitable organic solvent, and analysis of the extract by a capillary GC using an FID. Between 500 and 1000 L, air at a flow rate of 120 L/h is recommended for sampling, which can give a detection limit of 0.15–0.50 $\mu g/m^3$ for each compound (Riepe and Liphard, 1987). The method suggests the installation of an absorber resin, such as XAD-2 or Tenax, after the filter if PAH vapors were to be trapped (at temperature over 50°C). Cyclohexane or toluene is recommended as the desorption solvent.

Air analysis may be performed by the U.S. EPA Method TO13 (U.S. EPA 1988), which is quite similar to the above method. PAH-bound particles and vapors (many compounds may partially volatilize after collection) may be trapped on a filter and adsorbent (XAD-2, Tenax, or polyurethane foam), and then desorbed with a solvent. The solvent extract is then concentrated and analyzed by HPLC (UV/fluorescence detection), GC-FID, or GC/MS (preferably in SIM mode). Because of very low level of detection required for many carcinogenic PAHs, including benzo(*a*)pyrene, the method suggests the sampling of a very high volume of air (more than 300,000 L).

The analysis of PAH in air may be done by NIOSH Methods 5506 and 5515 (NIOSH, 1985). Air is passed over a sorbent filter consisting of PTFE and washed XAD-2. The sample volume and flow rate should be 200–1000 L and 2 L/min, respectively. The PAH compounds are extracted with a solvent and analyzed by HPLC using a UV or fluorescence detector. UV absorbance is set at 254 nm. A fluorescence detector is set at excitation 340 nm or emission 425 nm. The solvent extract may be alternatively analyzed by GC-FID using a capillary column.

REFERENCE

Riepe, W. and G. Liphard. 1987. *Handbook of Environmental Analysis*, 1st edn. Boca Raton, FL: CRC Press.

38 Nitrogen (Ammonia)

Ammonia, NH_3 [7664-41-7] is one of the most widely used chemicals having multiple industrial applications. It is used in the manufacture of fertilizers, nitric acid, explosives, synthetic fibers, urea, soda ash, dyes, amines, and many ammonium salts. Workers in these industries and also in many other areas, such as petroleum refining and glass cleaning, are susceptible to chronic exposure risks from ammonia. The Permissible Exposure Level (PEL) in the ambient air at the workplace for ammonia set by the Occupational Safety and Health Administration (OSHA) is 35 ppm (20 mg/m^3). It is the Short Term Exposure Limit (STEL). The Time Weighted Average (TWA) pertaining to an 8-hour working day/5-days a week is currently under review to be lowered to a concentration of 10 mg/m^3 that includes ammonia, ammonium chloride fume, or ammonium sulfamate. In this chapter, the analysis of ammonia both in water and air are presented. For the water analysis, ammonia is measured as the ammonia-nitrogen or nitrogen-ammonia (NH_3-N), and its concentration is expressed as the nitrogen equivalent of ammonia in mg/L of an aqueous sample. In air analysis, it is measured as ammonia or as the ammonium ion (NH_4^+), depending on the method of analysis, and the concentration is expressed as mg NH_3/m^3 of air or as part per million (ppm) equivalents.

Ammonia (NH_3) occurs in varying concentrations in groundwater, surface water, and wastewater. Its occurrence in water and sludge is primarily attributed to its formation resulting from the reduction of nitrogen-containing organics, deamination of amines, and hydrolysis of urea, and also to its use in water treatment plants for dechlorination. Its concentration in groundwater is relatively low because of its adsorption to soil.

Ammonia-nitrogen (NH_3-N) may be analyzed by the following methods:

1. Colorimetric Nesslerization method
2. Colorimetric phenate method
3. Titrimetric method
4. Ammonia-selective electrode method

Sample distillation is often required before analysis, especially for wastewater and sludge where the interference effect is significant. Distillation, however, may not be necessary for potable waters or clean and purified samples where the concentration of ammonia is expected to be low. When the titrimetric method is followed, the sample must be distilled.

SAMPLE DISTILLATION

Distillation of the sample is often necessary for the removal of interfering contaminants. The sample is buffered at pH 9.5 with the borate buffer prior to distillation. This decreases hydrolysis of cyanates (CNO^-) and organic nitrogen compounds.

Distillation is performed in a 2 L borosilicate glass apparatus, or an apparatus with aluminum or tin tubes as the condensing units. Before the sample is distilled, clean the apparatus until it is free from trace ammonia. This is done by distilling 500 mL NH_3-free distilled water containing 20 mL borate buffer and adjusted to pH 9.5 with NaOH.

To 500 mL sample, add 25 mL borate buffer and adjust the pH to 9.5 with 6 N NaOH. If there is residual chlorine in the sample, dechlorinate by treating with $Na_2S_2O_3$ before adding the borate buffer.

Distill the sample at a rate of 5–10 mL/min. Collect between 200 and 350 mL distillate over 50 mL of one of the following solutions, depending on the method of analysis:

- Boric acid—colorimetric Nesslerization method
- Boric acid-indicator solution—titrimetric analysis
- Sulfuric acid (0.05 N)—colorimetric phenate method or ammonia electrode method

Reagents

- Ammonia-free distilled water: pass distilled water through a strongly acidic cation-exchange resin. Alternatively, add a few drops of concentration H_2SO_4 and redistill.
- Borate buffer solution: to 9.5 g sodium tetraborate ($Na_2B_4O_7 \cdot 10\ H_2O$) in 500 mL water (0.025 M), add 88 mL 0.1 N NaOH solution and dilute to 1 L.
- Sodium thiosulfate: dissolve 3.5 g $Na_2S_2O_3 \cdot 5\ H_2O$ in 1 L water.
- Boric acid solution: 2 g boric acid in 100 mL water.

TITRIMETRIC METHOD

This method is based on the titration of basic ammonia with standard sulfuric acid using methyl red-methylene blue indicator to pale lavender end point. Distill 100 mL sample into 50 mL boric acid mixed indicator solution. Titrate ammonia in this distillate solution with standard H_2SO_4 (0.02 N) until the color turns to pale lavender. Perform a blank titration using the distillate obtained from the reagent grade water under similar conditions. Calculate the concentration of NH_3-N in the sample as follows:

$$\text{mg } NH_3\text{-N/L} = \frac{(V_s - V_b) \times 280}{\text{mL sample}}$$

where

V_s is mL H_2SO_4 required for the titration of sample distillate
V_b is mL H_2SO_4 required in the blank titration

Since normality of H_2SO_4 used is 0.02, which is equivalent to 0.02 N NH_3 solution or 0.02×17 g/L or 340 mg/L ammonia (because the equivalent weight of NH_3 is 17). This is equal to (340 mg/L×(14/17)) or 280 mg/L of nitrogen (because 1 mol of NH_3 contains 1 mol or 14 g N). If we use H_2SO_4 having a different normality in the titration, then substitute 280 with $140x$ in the calculation where x = normality of H_2SO_4.

Reagents

- Methyl red-methylene blue indicator solution: dissolve 200 mg methyl red in 100 mL 95% ethanol. Separately, dissolve 100 mg methylene blue in 50 mL 95% ethanol. Mix both these solutions.
- Boric acid-indicator solution: dissolve 20 g boric acid in distilled water. Add 10 mL methyl red-methylene blue indicator solution. Dilute to 1 L.
- Sulfuric acid standard (0.02 N): dilute 3 mL of concentrated H_2SO_4 to 1 L with CO_2-free distilled water. This solution would have a strength of approximately 0.1 N. Dilute 200 mL of this 0.1 N H_2SO_4 to 1 L with CO_2-free distilled water. Determine the normality of this solution by titrating with 0.02 N standard Na_2CO_3 solution using methyl red or methyl red-methylene blue indicator. Na_2CO_3 solution of 0.02 N is made by dissolving 1.060 g anhydrous Na_2CO_3 dried in an oven at 140°C, in distilled water, and diluted to 1 L.

Alternatively, standardize 0.1 N commercially available H_2SO_4 or the acid of same strength prepared above against 0.1 N Na_2CO_3 (5.300 g anhydrous Na_2CO_3 dissolved in distilled water and diluted to 1 L) using methyl red indicator (the color changes from pink to yellow at the end point) or methyl red-methylene blue indicator.

$$\text{Normality of } H_2SO_4 = \frac{\text{mL } Na_2CO_3 \text{ titrant (blank subtracted)} \times 0.1\text{N}}{\text{mL } H_2SO_4 \text{ taken}}$$

Dilute 200 mL of H_2SO_4 standardized above 1 L, which should give normality in the range 0.02. Record the exact strength of this solution.

Standardization of 0.1 N H_2SO_4 may alternatively be performed by potentiometric titration to pH of about 5 using Na_2CO_3 standard.

COLORIMETRIC NESSLERIZATION METHOD

Clean samples may be directly analyzed by this method without distillation. However, a distillate portion should be analyzed for samples containing colored matters, or in the presence of interferences.

Under alkaline conditions, the Nessler reagent reacts with ammonia to produce a yellow mercuric salt. The intensity of the color produced is proportional to the concentration of ammonia in the sample. The reaction is as follows:

$$2K_2HgI_4 + NH_3 + 3KOH \rightarrow Hg_2OINH_2 + 7KI + 2H_2O$$

Procedure

If undistilled sample is used, the addition of zinc sulfate in the presence of NaOH would precipitate out iron, magnesium, calcium, and sulfide as a heavy flocculent, leaving a clear and colorless supernate. To 100 mL sample, add 1 mL $ZnSO_4$ solution and mix. Add 0.5 mL NaOH solution. Adjust the pH to 10.5 by further addition of NaOH solution, if needed. Filter out any heavy flocculent precipitate formed. Discard the first 20 mL filtrate. To 50 mL filtrate, add one drop of EDTA reagent. If Ca^{2+}, Mg^{2+}, or other metal ions are present in the sample, the EDTA would form salts with these ions, thus preventing their reaction with the Nessler reagent. After this, add 2 mL of the Nessler reagent and mix. Allow the mixture to stand for 10 min. Measure the absorbance or transmittance of the color developed. Measure the color of the blank and standards.

If the sample is distilled, neutralize a 50 mL portion of boric acid distillate with NaOH and then add 1 mL Nessler reagent. Let the solution stand for 10 min, after which measure the absorbance or transmittance against a reagent blank. Prepare a calibration curve under the same conditions as samples. The reagent blank and the standards should be distilled, neutralized, and Nesslerized before color measurements.

Calculation

For undistilled sample,

$$\text{mg } NH_3\text{-N/L} = \frac{\mu\text{g } NH_3\text{ - N read from calibration curve}}{\text{mL of pretreated sample taken}}$$

When the sample is distilled,

$$\text{mg } NH_3\text{-N/L} = \frac{\mu\text{g } NH_3\text{-N read from the curve}}{\text{mL of original sample} \times (V_1/V_2)}$$

where

V_1 is the total volume of distillate collected, mL (including boric acid adsorbent)

V_2 is the mL distillate portion taken for Nesslerization

Reagents and Standards

- Use ammonia-free distilled water in the preparation of all the reagents and standards.
- Nessler reagent: dissolve 100 g HgI_2 and 70 g KI in 250 mL distilled water. Add this mixture slowly with stirring to a solution of NaOH (160 g in 500 mL distilled water). Dilute to 1 L.
- EDTA reagent: add 50 g disodium ethylenediamine tetraacetate dihydrate to 100 mL of 10% NaOH solution (10 g NaOH/100 mL distilled water). Heat if necessary to dissolve.
- Zinc sulfate solution: dissolve 10 g $ZnSO_4 \cdot 7\ H_2O$ in distilled water and dilute to 100 mL.
- Ammonia-nitrogen standards: dissolve 3.819 g anhydrous NH_4Cl, dried at 100°C, in distilled water and dilute to 1 L. The strength of this solution is 1000 mg NH_3-N/L or 1 mL = 1 mg NH_3-N = 1.22 mg NH_3.

Dilute 10 mL of stock solution prepared as above to 1 L. The strength of this secondary standard is 10 mg NH_3-N/L or 1 mL = 10 μg NH_3-N = 12.2 μg NH_3.

Prepare a series of Nessler tube standards as follows:

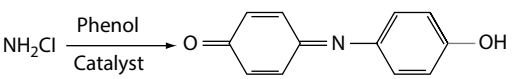
Secondary Standard Taken (mL)	NH_3-N/50 mL (μg)
0.0	0.0
1.0	10.0
2.0	20.0
4.0	40.0
6.0	60.0
8.0	80.0
10.0	100.0

COLORIMETRIC PHENATE METHOD

Ammonia reacts with hypochlorite to form monochloroamine. The latter reacts with phenol to form an intensely blue compound, indophenol. The reaction is catalyzed by $MnSO_4$. The reaction steps are as follows:

$$NH_3 + OCl^- \rightarrow NH_2Cl + OH^-$$

(Monochloroamine)



(Indophenol)

The intensity of the color developed, which depends on the amount of indophenol produced, is proportional to the concentration of the ammonia in the sample. The intensity of the color is measured by a spectrophotometer or a filter photometer (providing a light path of 1 cm) at 630 nm. The concentration of NH_3-N is determined from a calibration standard curve.

Procedure

Take 10 mL sample in a beaker and place it on a magnetic stirrer. Add one drop of $MnSO_4$ solution. Add 0.5 mL hypochlorous acid reagent, followed by immediate addition of 0.5 mL (10 drops) phenate reagent dropwise while stirring vigorously. Allow the solution to stand for 10 min for maximum color development. Read the absorbance at 630 nm after zeroing the spectrophotometer to reagent blank. Run a distilled water blank following the same procedure. Prior to the sample analysis, prepare a calibration standard curve following exactly the above procedure. Run one of the standards through the procedure with each batch of the sample.

Calculation

$$\text{mg } NH_3\text{-N/L} = \frac{\text{mg } NH_3\text{-N read from the standard curve}}{\text{mL sample used}} \times 1000$$

If the results are to be expressed in mg/L, the above equation simplifies to

$$\text{mg } NH_3\text{-N/L} = \frac{\text{mg } NH_3\text{-N read from the standard curve}}{\text{mL sample used}}$$

In routine analysis, one standard may be run in a batch to check the calibration curve. Within a linear range, the concentration of NH_3-N in the sample may be determined from a single standard as follows:

$$\text{mg } NH_3\text{-N/L} = \frac{A \times B}{C \times S}$$

where

A is the absorbance of sample
B is the μg NH_3-N in standard
C is the absorbance of standard
S is the mL sample used

Subtract any blank value, if positive, from the result.

If the sample is turbid or colored or has a high alkalinity (>500 mg $CaCO_3$/L), distill the sample and use a portion of the distillate. When the sample distillate is used in the analysis, multiply the result by V_1/V_2, where V_1 is mL of total distillate collected and V_2 is mL distillate used for color development. Use any one of the above equations in the calculation.

Reagents and Standards

- Phenate reagent: dissolve 2.5 g NaOH and 10 g phenol in 100 mL distilled water.
- Hypochlorous acid: add 5 mL of 5%–6% NaOCl solution to 20 mL water. Adjust pH to 6.5–7.0 with HCl. The reagent is unstable after a week.
- Manganous sulfate solution (0.003 M): 50 mg $MnSO_4 \cdot H_2O$ in 100 mL water.

- Calibration standards: prepare the stock NH_3-N standard solution by dissolving 0.382 g anhydrous NH_4Cl, dried at 100°C in distilled ammonia-free water, and diluting to 1 L. The strength of this solution is 122 μg NH_3/mL = 100 μg N/mL.
- Secondary standard is made by diluting 5 mL stock solution to 1000 mL. The strength of this solution is 0.500 μg N/mL or 0.605 μg NH_3/mL.
- Prepare the calibration curve using the following standards and record the corresponding absorbance plot of absorbance against μg NH_3-N in the standards.

Taken in Beaker	Microgram Mass of NH_3-N Present
0.5 mL secondary std. diluted to 10 mL	0.25
1 mL secondary std. + 9 mL water	0.50
2 mL secondary std. + 8 mL water	1.0
5 mL secondary std. + 5 mL water	2.5
10 mL secondary std. + no water	5.0

ION-SELECTIVE ELECTRODE

This method can measure the concentration of NH_3-N in water in the range of 0.03–1400 mg/L. Color and turbidity do not affect the measurement. Distillation of the sample, therefore, is not necessary. High concentration of dissolved solids in the sample, however, can cause error. In addition, certain complex forming ions, such as mercury or silver, which form complexes with ammonia, interfere with the test. The presence of amines in the sample can give high values.

Use an ammonia electrode (Orion Model 95–10, Beckman Model 39565 or equivalent) along with a readout device, such as a pH meter with an expanded millivolt scale between −700 and +700 mV or a specific ion meter. The electrode assembly consists of a sensor glass electrode and a reference electrode mounted behind a hydrophobic gas-permeable membrane. The membrane separates the aqueous sample from an ammonium chloride internal solution. Before analysis, the sample is treated with caustic soda to convert any NH_4^+ ions present in the sample into NH_3. The dissolved NH_3 in the sample diffuses through the membrane until the partial pressure of NH_3 in the sample becomes equal to that in the internal solution. The partial pressure of ammonia is proportional to its concentration in the sample. The diffusion of NH_3 into the internal solution increases its pH, which is measured by a pH electrode. The chloride level in the internal standard solution remains constant. It is sensed by a chloride ion-selective electrode that serves as the reference electrode.

Procedure

Follow the manufacturer's instructions for the operation of the electrode.

Prepare a series of NH_3-N standards from the stock solution covering the expected range of its concentrations in the samples. Place 100 mL of each standard solution in 150 mL beakers. To calibrate the electrometer, immerse the electrode into the lowest standard first and add 1 mL of 10 N NaOH. This should raise the pH of the solution to above 11. Add NaOH solution only after immersing the electrode.

Stir the solution throughout the measurements at a low but constant rate using a magnetic stirrer. Maintain a constant temperature throughout. Record the millivolt reading when the solution is stable. Repeat this procedure with the remaining standard, measuring the millivolt reading for each standard, proceeding from the lowest to the highest concentration.

Prepare a calibration curve on a semilogarithmic paper, plotting concentrations of NH_3-N against their corresponding response in millivolts. Plot the concentrations on the log axis and millivolts on the linear axis.

Record the potentials in millivolts for samples (using 100 mL aliquots or portions diluted to 100 mL for highly concentrated samples) using the above procedure. Determine the concentration of NH_3-N in the samples from the calibration curve. If the samples were diluted, multiply the results by the dilution factors.

Alternatively, the analysis may be performed by the standard addition method (see Chapter 9) in which no calibration curve is required. Prepare an NH_3 standard solution that is about 10 times as concentrated as the estimated concentration of NH_3-N in the sample. Determine the electrode slope following the instruction manual. To 100 mL sample, add 1 mL of 10 N NaOH and immerse the electrode and stir the solution. Record the millivolt value E_1 when the reading is stable. Add 10 mL of standard solution into the sample. Mix thoroughly and record the stable millivolt reading E_2. Calculate the millivolt difference ΔE as $E_2 - E_1$ and determine the concentration, C_x mg NH_3-N/L, from the following expression:

$$C_x = Q \times C_y$$

where

C_y is the concentration of added standard

Q is a reading corresponding to ΔE value that may be found in the known addition table (given in the instruction manual for the electrode)

C_x alternatively may be calculated from the following equation:

$$C_x = \frac{\rho C_y}{[(1+\rho) \times 10^{\Delta E/S} - 1]}$$

where

ρ is the ratio of the volume of spiked standard to the volume of sample taken

S is the electrode slope (see Chapter 9 for a typical calculation)

Reagents and Standards

- Use NH_3-free distilled water to prepare all reagents and standards.
- 10 N NaOH: dissolve 40 g NaOH in distilled water and dilute to 100 mL.
- NH_3-N standard: dissolve 3.819 g anhydrous NH_4Cl in distilled water and dilute to 1 L. Concentration of this solution is 1000 mg NH_3-N/L. Prepare 0.1, 1, 10, and 100 mg/L standards by dilutions. Prepare the calibration curve in the concentration range 0.1–1000 mg NH_3-N/L.

AIR ANALYSIS

Ammonia in indoor air can be measured by several methods including the OSHA Method, ID-188, and the NIOSH Method 6015. These methods include sampling a measured volume of air using a personal sampling pump and adsorbent tubes followed by desorption and analysis. In the OSHA Method, a known volume of air, recommended 24 L (for TWA) at a flow rate of 0.10 L/min or 7.5 L (for STEL) at a flow rate of 0.5 L/min is drawn through a glass tube containing carbon beads impregnated with sulfuric acid. Ammonia is converted into ammonium sulfate, $(NH_4)^2SO_4$. The sample is desorbed with a known volume of de-ionized water and analyzed as ammonium ion, NH_4+ by

ion chromatography using an appropriate cation exchange resin column. To measure ammonium chloride, NH_4Cl [12125] and ammonium sulfamate [7773-06-0] samples are collected on a 0.8 μm mixed-cellulose ester filter, desorbed with de-ionized water and analyzed by ion chromatography as an NH4+ ion.

An earlier method involved drawing a measured volume of air through a midget fritted glass bubbler containing 0.1 N H_2SO_4 and analyzing solution for ammonia either by colorimetry with Nessler's reagent or by ion selective electrode (ISE) for an ammonium ion. Such a colorimetric procedure, however, is susceptible to interference. The ISE analysis does not distinguish between ammonia and amines.

The NIOSH Method 6015 uses solid sorbent tubes packed with H_2SO_4-treated silica gel. Air is drawn at a flow rate of 0.1–0.2 L/min. The sorbent material is extracted with 20 mL de-ionized water, followed by converting ammonia into indophenol blue by treating with the appropriate color developing mixture and measuring absorbance by visible absorption spectrophotometry at 630–660 nm. The color developing solution is made by mixing EDTA anti-precipitant, phenolate coupling agent, sodium nitroprusside intensifier, and sodium hypochlorite.

REFERENCES

OSHA Analytical Methods Manual. 2002. *Method Number ID-188*. Occupational Safety and Health Administration, Industrial Hygiene Chemistry Division, OSHA Salt Lake Technical Center, Sandy, Utah.

NIOSH Analytical Method 6015. 1994. *NIOSH Manual of Analytical Methods*. Cincinnati, OH: National Institute for Occupational Safety and Health.

39 Nitrogen (Nitrate)

Many nitrate minerals occur in nature, such as potassium nitrate, KNO_3 or saltpeter, and sodium nitrate, $NaNO_3$ or Peru saltpeter. Nitrate salts have wide industrial applications. They are used as fertilizers in agriculture, and are also common laboratory chemicals. Nitrates are ubiquitously found in the environment at low concentrations. In the soil, various forms of nitrogen produced from decaying of plants and animal residues and also from other sources can convert by bacteria into nitrate, NO_3^- and nitrite, NO_2^- ions. In environmental analysis, the concentration of nitrogen is generally expressed as nitrate-nitrogen, NO_3^--N, which refers to nitrogen equivalents of nitrate. Thus, 1 mg NO_3^--N is equal to 4.426 mg NO_3^-.

Nitrate, which is produced by oxidation of nitrogen, is a monovalent polyanion having the formula NO_3^-. Most metal nitrates are soluble in water and occur in trace amounts in surface- and groundwater. Nitrate is toxic to human health and chronic exposure to high concentrations of nitrate may cause methemoglobinemia. The maximum contaminant limit in potable water imposed by the U.S. EPA is 10 mg nitrate as nitrogen/L.

Nitrates in water may be analyzed by the following methods:

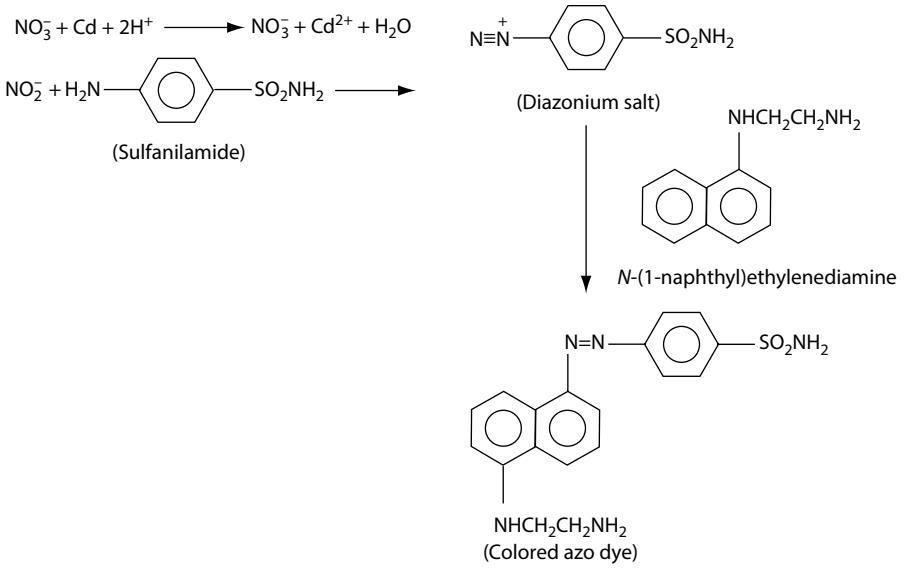
1. Ion chromatography
2. Nitrate selective electrode method
3. Cadmium reduction method
4. Miscellaneous reduction method
5. Brucine method

Methods 3 and 4 are colorimetric procedures based on the reduction of nitrate to nitrite, followed by diazotization and then coupling to an azo dye. The analysis may be performed manually or by use of an automated analyzer. Method 2 is applicable in the range of 10^{-5}–10^{-1} M NO_3^-. The colorimetric method 5 has been found to give inconsistent results.

CADMIUM REDUCTION METHOD

In the presence of cadmium, nitrate (NO_3^-) is reduced to nitrite (NO_2^-). The nitrite produced is diazotized with sulfanilamide. This is followed by coupling with *N*-(1-naphthyl)-ethylenediamine to form a highly colored azo dye. The intensity of the color developed is measured by a spectrophotometer or a filter photometer at 540 nm. The concentration of oxidized N/L (NO_3^+-N plus NO_2^--N) is read from a standard curve prepared by plotting the absorbance (or transmittance) of the standard against NO_3^--N concentrations.

The reactions are as follows:



Nitrite is determined separately by the colorimetric method on another aliquot of the sample not subjected to Cd reduction. Subtract NO_2^--N value to determine the concentration of NO_3^--N in the sample.

Procedure

Mix 25 mL sample with 75 mL of the NH_4Cl–EDTA solution. The sample mixture is passed through the cadmium column at a rate of 5–10 mL/min. This reduces nitrate to nitrite. Discard the first 25 mL and collect the remaining solution.

To 50 mL of the solution passed through the cadmium column, add 2 mL of color reagent and mix. Allow the solution to stand for 30 min. Measure the absorbance at 543 nm against a distilled water–reagent blank. Read the concentration of NO_3^--N from the prepared standard curve. Standards should be reduced exactly like samples.

Apparatus, Reagents, and Standards

- Cadmium column: insert glass wool plug at the bottom of the column. Add Cd–Cu granules into the column producing a height of 18.5 cm. Fill the column with water and maintain water level above the granules to prevent any entrapment of air. Wash the column with a dilute solution of NH_4Cl–EDTA. Before beginning the analysis, activate the column bypassing 100 mL solution containing 1 mg NO_3^--N standard in the NH_4Cl–EDTA solution (25:75).
- Ammonium chloride–EDTA solution: dissolve NH_4Cl (13 g) and disodium EDTA (1.7 g) in the groundwater. Adjust the pH to 8.5 with the concentration of NH_4OH and dilute to 1 L.
- Color reagent: dissolve 10 g sulfanilamide in dilute phosphoric acid solution (100 mL 85% H_3PO_4 in 800 mL water). Add 1 g *N*-(1-naphthyl) ethylenediamine dihydrochloride into this solution. Mix well and dilute to 1 L.
- Standards: dissolve 7 g dried potassium nitrate (KNO_3) in distilled water and dilute to 1 L [1 mL + 1 mg (1000 ppm)]. Dilute 10 mL of the above stock solution to 1 L to produce a secondary standard, 10 mg NO_3^--N/L.

Dilute 0.5, 1.0, 2.0, 5.0, and 10.0 mL of the secondary standard to 100 mL, respectively. This would give a series of standards of strength 0.05, 0.1, 0.2, 0.5, and 1.0 mg of NO_3^--N/L, respectively. Check the efficiency of the column by comparing one of the reduced nitrate standards to a nitrite standard at the same concentration. If the reduction efficiency falls below 75%, use freshly prepared CuCd granules.

- Copper–cadmium granules: mix 25 g 40–60 mesh Cd granules with 6 N HCl and shake well. Decant off HCl and rinse the granules with distilled water. Add 100 mL 2% $CuSO_4$ solution to the cadmium granules. Swirl for 5–7 min. Decant and repeat this step with fresh $CuSO_4$ solutions until a brown colloidal precipitate of Cu appears. Wash out the precipitate with water.

MISCELLANEOUS REDUCTION METHOD

Reducing agents other than Cd may be used to convert nitrate to nitrite. Some of those agents are hydrazine sulfate ($N_2H_4 \cdot H_2SO_4$), titanous chloride ($TiCl_3$), and stannous chloride ($SnCl_2$). The nitrite formed is diazotized with sulfanilamide and coupled with *N*-(1-naphthyl) ethylenediamine dihydrochloride to form a highly colored azo dye, the absorbance of which may be measured by a spectrophotometer. A calibration curve is plotted using the NO_3^--N standards subjected to similar reduction. Nitrite is determined separately without reduction, and the value is subtracted from the total nitrate and nitrite as analyzed after the reduction.

NITRATE ELECTRODE METHOD

Nitrate in water may be analyzed by using a nitrate selective sensor. Chloride and bicarbonate ions at concentrations about 10 times greater than nitrate interfere in this test. Sulfide, cyanide, and halide ions are eliminated by using a buffer solution containing $AgSO_4$. The buffer, boric acid at pH 3, removes the bicarbonate.

Procedure

Prepare three nitrate standards at concentrations 1, 10, and 50 mg/L. To 10 mL of each standard in 40 mL beakers, add 10 mL buffer solution, respectively. Immerse the tip of the electrode in the solution while stirring. Record the stable millivolt reading for each standard. Prepare a calibration curve plotting NO_3^--N concentrations in the abscissa and millivolts in the ordinate. The plot should be a straight line with a slope of 57 ± 3 mV/decade at 25°C. After this, rinse and dry the electrode; immerse in the sample–buffer mixture and record the stable potential reading. Determine the concentration of NO_3^--N in the sample from the calibration curve.

Reagents

- Buffer solution: dissolve the following reagents in 700–800 mL of distilled water: 17.3 g Al_2SO_4, 1.3 g boric acid, and 2.5 g sulfamic acid. Add 0.10 N NaOH slowly to adjust the pH to 3.0. Dilute to 1 L and store in a dark bottle.
- Reference electrode filling solution: 0.53 g $(NH_4)_2SO_4$ in 1 L distilled water.

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40 Nitrosamines

Many nitrosamines may also contain other functional groups, instead of alkyl or aryl groups, such as alcohol. For example, in N-nitrosodiethanolamine, $(HOCH_2CH_2)_2N{-}N{=}O$ [1116-54-7], there are two ethanol substitutions on the nitrogen atom attached to the nitroso group. In general, nitrosamines are produced by the reaction of nitrite ion, NO_2^- or any nitrosating agent with a secondary or tertiary amine, R_2NH or R_3N. Thus, nitrate ion, NO_3^- that commonly occurs in many environmental matrices is susceptible to reduce first to nitrite and then to nitrosamine: nitrate → nitrite → nitrosamine. Nitrite ion and nitrous acid, HNO_2 both are, however, weak nitrosating agents. The formation of nitrosamines therefore may involve the following steps:

$$NO_2^- + H^+ \rightarrow HNO_2$$
$$2HNO_2 \rightarrow N_2O_3 + H_2O$$
$$R_1R_2NH + N_2O_3 \rightarrow R_1R_2N{-}N{=}O$$

Since the acidic conditions favor the formation of N-nitroso compounds, they may form *in vivo* in the stomach. They may form in the food during storage. Similarly, in the environmental waters or soils under reducing conditions and at low pH, these compounds are susceptible to form. Nitrosamines occur in a wide variety of foods, natural products, agricultural chemicals, cutting fluids, tanned leather, and rubber additives.

Nitrosamines or nitrosoamines are nitroso derivatives of amines in which a nitroso (NO) group is attached to the nitrogen atom of the amine. These compounds have the following general structure: $R_2N{-}N{=}O$, where R is an alkyl or aryl group.

Nitrosamines are toxic compounds as well as potent animal and human carcinogens (Patnaik, 2007). These substances occur in trace quantities in tobacco smoke, meat products, and salted fish. The U.S. EPA classifies some of these compounds as priority pollutants in industrial wastewater, potable water, and hazardous waste. These nitrosamines are listed in Tables 40.1 and 40.2. Such pollutants occurring in environmental samples can be determined by U.S. EPA's analytical procedures (U.S. EPA, 1992, 2004).

The separation of nitrosamines from various types of sample matrices described in the literature involves liquid–liquid extraction, solid-phase extraction, supercritical fluid extraction using supercritical CO_2, and low-temperature distillation techniques. The instrumental analysis can be performed by GC, reversed-phase HPLC, and GC/MS, as well as LC/MS, both at low or high resolution. For less volatile or thermally unstable compounds, however, liquid chromatography offers advantages over gas chromatography. However, in environmental analysis, the nitrosamines that are mostly determined are compounds of low molecular masses and are volatile under the GC conditions and therefore can be conveniently analyzed by GC.

The analysis involves the extraction of these compounds into a suitable solvent followed by their detection on the GC by using either a NPD, or a reductive HECD, or a thermal energy analyzer (TEA). These compounds can also be detected by a FID, but at a lower sensitivity. For example, the detector response to the lowest amount of *N*-nitrosodi-*n*-propylamine on FID is in the range 200 ng, in comparison to 5 ng on the NPD. When interferences are encountered, TEA or a reductive HECD should be used for the analysis. Both of these detectors offer high sensitivity and selectivity. The presence of nitrosamines in the sample extract must be confirmed either on a GC using a second column or by GC/MS, preferably under high-resolution MS conditions. *N*-Nitrosodiphenylamine breaks down to diphenylamine, at a temperature above 200°C in the GC inlet and it is measured

TABLE 40.1
Nitrosamines Classified as Priority Pollutants by U.S. EPA under the Resource Conservation and Recovery Act

CAS No.	Compound
[62-75-9]	*N*-Nitrosodimethylamine[a]
[10595-95-6]	*N*-Nitrosomethylethylamine
[55-18-5]	*N*-Nitrosodiethylamine
[621-64-7]	*N*-Nitrosododi-*n*-propylamine[a]
[924-16-3]	*N*-Nitrosodibutylamine
[86-30-6]	*N*-Nitrosodiphenylamine[a]
[100-75-4]	*N*-Nitrosopiperidine
[930-55-2]	*N*-Nitrosopyrrolidine
[59-89-2]	*N*-Nitrosomorpholine

[a] Also classified as pollutants in the wastewater category.

TABLE 40.2
Characteristic Masses for Some Common Nitrosamine Pollutants

Compounds	Primary Ion (*m/z*)	Secondary Ions (*m/z*)
N-Nitrosodimethylamine	42	74, 44
N-Nitrosomethylethylamine	88	42, 43, 56
N-Nitrosodiethylamine	102	42, 57, 44, 56
N-Nitrosodi-*n*-propylamine	70	42, 101, 130
N-Nitrosodibutylamine	84	57, 41, 116, 158
N-Nitrosodiamylamine	98	57, 41, 186
N-Nitrosodiphenylamine[a]	169	168, 167
N-Nitrosopiperidine	114	42, 55, 56, 41
N-Nitrosopyrrolidine	100	41, 42, 68, 69

[a] Diphenylamine produces the same characteristic ions.

as diphenylamine. If present in the sample, the latter compound, must, therefore, be removed by Florisil or alumina cleanup before analysis.

EXTRACTION

A 1 L aliquot, or any appropriate volume of accurately measured aqueous sample, is extracted with methylene chloride by liquid–liquid extraction. The extract is concentrated to 1 mL or any small volume on a Kuderna–Danish setup. A Florisil column cleanup may be necessary if the sample is dirty, or the presence of interferences is known or suspected or if *N*-nitrosodiphenylamine is to be determined.

Soil, sediments, and hazardous waste should be extracted with methylene chloride by sonication or Soxhlet extraction. The extract is then concentrated and cleaned up for the removal of interferences as follows.

Prior to the Florisil column cleanup, the column should be pre-eluted with an ether–pentane mixture (15:85 v/v). The extract is then transferred onto the column and the column is eluted again

to remove any diphenylamine contaminant. The analytes *N*-nitrosodimethylamine, *N*-nitrosodi-*n*-propylamine, and *N*-nitrosodiphenylamine, and other similar aliphatic and aromatic nitrosamines are desorbed from the column with the acetone–ether mixture (5:95 v/v). This fraction is then concentrated for analysis.

In the alumina column cleanup, the column is first pre-eluted with the ether–pentane mixture (30:70) before the sample extract is transferred onto the column. It is then successively eluted with the ether–pentane mixture of 30%:70% and 50%:50% composition, respectively. This separates the *N*-nitrosodiphenylamine. The latter elutes into the first fraction, from the interfering substance diphenylamine that goes into the second fraction along with the analytes, *N*-nitrosodimethylamine and *N*-nitrosodi-*n*-propylamine. A small amount of the latter compound is also eluted into the first fraction. A cleanup procedure for other nitrosamines (not classified under U.S. EPA's priority pollutants) should generally be the same as described above. The composition of the ether–pentane mixture and the elution pattern, however, must be established first before performing the cleanup.

ANALYSIS

The sample extract is analyzed by GC-NPD and/or GC/MS. Other GC detectors, as mentioned earlier, may be used instead of NPD. If low detection level is desired, quantitation should be done from the GC analysis. The presence of any analyte found in the sample must be confirmed on an alternate GC column or preferably by GC/MS. If a thermoionic detector is used and if the sample extract is to be analyzed without any cleanup, it is necessary to exchange the solvent from methylene chloride to methanol.

Column and conditions are as follows:

- Packed column: 1.8 m × 4 mm ID glass packed with (1) 10% Carbowax 20 M/2% KOH on Chromosorb W-AW (80/100 mesh) or (2) 10% SP-2250 on Supelcoport (100/120 mesh) or equivalent at 110–220°C at 8°C/min, with the carrier gas at 40 mL/min flow rate.
- Capillary column: fused silica capillary column, such as RTX-5, DB-5, SPB-5, or equivalent, 15 m × 0.53 mm ID × 1.5 μm film (direct injection) at 40–240°C at H_2 carrier gas linear velocity 80 cm/s (or flow rate 10 mL/min). A longer column 30 m with smaller ID and lesser film thickness may be used with split injection. Temperature and carrier-gas flow conditions may be set accordingly.

The characteristic ions for GC/MS identification (under electron impact ionization at 70 eV nominal energy) for some common nitrosamine pollutants are tabulated in Table 40.2.

US EPA Method 521 (U.S. EPA, 2004) discusses an analytical procedure to measure nitrosamines in drinking water. The method is based on SPE of water and analysis by chemical ionization mass spectrometry.

AIR ANALYSIS

Nitrosamines in air may be analyzed by NIOSH Method 2522 (NIOSH, 1989). Air at a flow rate between 0.2 and 2 L/min is passed through a solid sorbent tube containing Thermosorb/N as an adsorbent. The sample volume should be between 15 and 1000 L. If high concentrations of nitrosamines are expected, another backup Thermosorb/N tube should be used in sampling. The sorbent tube, however, can adsorb the analytes up to 1500 μg loading with no breakthrough. The analytes are desorbed with 2 mL methanol–methylene chloride mixture (1:3), allowed to stand for 30 min, and analyzed by GC using a TEA. The column and conditions employed in the method development are as follows:

- Column: stainless steel, 10″ × 1/8″ packed with 10% Carbowax 20 M + 2% KOH on Chromosorb W-AW.

- Temperature: injector 200°C, detector 550–600°C, column 110–200°C at 5°C/min.
- Gases: N_2 carrier, 25 mL/min; oxygen, 5 mL/min; ozone 0.2 mL/min.
- U.S. EPA Method TO7 describes the determination of *N*-nitrosodimethylamine in ambient air (U.S. EPA, 1986). The method is similar to the NIOSH method discussed above and uses Thermosorb/N as adsorbent. The airflow is 2 L/min and the sample volume recommended is 300 L air. The analyte is desorbed with methylene chloride and determined by GC/MS or an alternate selective GC system, such as TEA, HECD, or thermoionic nitrogen-selective detector. The latter detector and the TEA are more sensitive and selective than the other detectors. Therefore, the interference from other substances is minimal. Other nitrosamines in air may be determined in the same way.

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41 Oil and Grease

The term oil and grease refers to neither a broad group of substances nor to any individual compound or specific group of substances with similar chemical structures or properties. Although the term is defined as all materials that may be recovered from the sample matrices when extracted by a suitable organic solvent and therefore is specific to a method or the solvent in use, in a broader sense of the term it generally infers to the oily and greasy materials that are mostly biological lipids and/or mineral hydrocarbons. Several solvents are known for their extraction efficiency. They include petroleum ether, trichlorotrifluoroethane, hexane, and hexane–MTBE mixtures. Thus, the substances recovered may vary from solvent to solvent. The use of fluorochlorocarbon solvent has been discontinued because of its harmful effects on the environment. Oil and grease in aqueous samples can be determined by the following methods:

1. Partition-gravimetric method
2. Partition-infrared method
3. Soxhlet extraction method
4. Solid phase partition-gravimetric method

These methods are briefly outlined below. The detailed procedures are described in the literature APHA, AWWA, and WEF (2005) and U.S. EPA (1995). The selection of the method depends on several factors including the nature of the sample, volatile substances present in the sample, the availability of materials and equipment for analysis, and the time and cost of analysis. Gravimetric procedures are always time consuming. It may be noted here that gravimetric measurements are susceptible to errors; weighing especially has to be very accurate in gravimetry and the cycle of heating and cooling of the crucible and the residues must be continued until constant weights are attained. The first two methods, the partition-gravimetry and the partition-infrared methods are based on liquid–liquid extraction. In these extractions, oil and grease materials which include biological lipids and mineral hydrocarbons are extracted from water into a suitable solvent that provides much greater solubility over water. All the methods mentioned above, however, may produce error in measuring volatile hydrocarbons such as short-chain hydrocarbons and simple aromatics. In gravimetric procedures, unsaturated fats and fatty acids in the sample may oxidize during evaporation steps.

PARTITION-GRAVIMETRY METHOD

Aqueous samples are acidified to a pH below 2 with either 1:1 HCl or H_2SO_4. Usually, 5 mL of acid should be sufficient for acidifying 1 L of sample. The sample measured to a volume of 1 L is then transferred into a 2 L separatory funnel. The sample bottle is rinsed with 30 mL extracting solvent and the solvent washings are added to the sample in the separatory funnel. The sample–solvent mixture is then shaken vigorously for 2 min. Allow the layers to separate. If the extracting organic solvent is lighter than water, such as hexane, then it will be on top of the water. If the solvent is heavier than water, then it will be in the bottom immiscible layer. The organic layer is then drained out carefully from the aqueous phase leaving a small amount of it in the water and passed through a funnel containing a filter paper and 10 g anhydrous sodium sulfate, both of which have been solvent-rinsed into a clean and tared distilling flask containing a few boiling chips. Passage through anhydrous Na_2SO_4 removes any trace waters present in the organic solvent extract.

To the aqueous layer another 30 mL organic solvent is now added, the mixture is shaken vigorously and the above steps are repeated. This is the second extraction. A third extraction is carried

out in the same way and all the solvent extracts are combined together in the distilling flask. A larger volume of the extracting solvent and repeated extractions always enhance the degree of partition of the organic substances into the solvent and therefore should ensure better removal of oil and grease materials from the water. Often emulsions form between the aqueous and the organic interface. Passing the emulsion and the solvent layer through the bed of anhydrous Na_2SO_4 can break such an emulsion. Alternatively, if the emulsion is greater than 5 mL the organic layer and the emulsion may be drained into a glass centrifuge tube and centrifuged for 5 min at 2400 rpm to separate out the clear organic phase. The mixture is then transferred into a separatory funnel to remove the clear organic phase.

The solvent is recovered from the combined extracts by distillation at 85°C in a water bath. When the distillation stops, pass air through the flask applying mild vacuum. Moisture adhering onto the outside of the flask is wiped and the flask with the residues is cooled in a desiccator until a constant weigh is obtained. QC check samples are commercially available to measure the precision and accuracy of the measurement. Alternatively, oil and grease standards can be prepared in the laboratory from hexadecane and stearic acid mixtures dissolved in the acetone.

Calculation

$$\text{Oil and grease, mg/L} = \frac{\text{Weight of dry residue (oil and grease), mg}}{\text{Sample volume, L}}$$

PARTITION-INFRARED METHOD

This method can be applied to measure oil and grease that also contains certain volatile hydrocarbons by an IR spectrophotometer. A major advantage of this method over the gravimetric measurement is that the total oil and grease measured by this method also includes its volatile hydrocarbon contents, which cannot be determined by gravimetric analysis where the solvent extracts are evaporated to dryness. In addition, this method gives a lower detection level. A major drawback of this method, however, is the presence of trichlorofluoroethane, a solvent harmful to the environment as the extraction solvent. Alternative solvents of nonhydrocarbon types with equivalent solubility and extraction efficiency, however, can be used instead of trichlorofluoroethane.

A 1 L of aqueous sample is transferred into a 2 L separatory funnel and shaken vigorously for 2 min with 30 mL trichlorofluoroethane. Pass the bottom solvent layer through 10 g anhydrous Na_2SO_4 placed on a filter paper in a funnel into a clean 100 mL volumetric flask. Both the filter paper and Na_2SO_4 should be prerinsed with the solvent prior to passing the solvent extract. The sample is extracted twice more with 30 mL of solvent each and the extracts are collected in the same flask. The final volume of the combined extracts in the volumetric flask is adjusted to 100 mL with the solvent. The calibration standard solutions are prepared from the reference oil made out of 37.5% isooctane, 37.5% hexadecane, and 25% benzene by volume and diluted in the solvent, trichlorofluoroethane accordingly. The working range of such calibration standards should fall between 4 and 40 mg. Scan the calibration standards and the sample from 3200 to 2700/cm with the solvent in the reference beam using a pair of matched near-IR silica cells of 1 cm path length. Measure the absorbance of the peak maximum at 2930/cm. Dilute the solution or select a shorter path length if the absorbance exceeds 0.8. Read the concentration of oil and grease in the sample from the calibration standard curve.

$$\text{Oil and grease, mg/L} = \frac{A \times 1000}{\text{mL sample}}$$

(where A = mg oil and grease in the extract determined from the calibration standard curve)

SOLID PHASE PARTITION-GRAVIMETRIC METHOD

In this method, oil and grease is separated from the aqueous sample by adsorption on a solid phase adsorbent. The aqueous sample is passed through a SPE disk, and the oil and grease substances partition and adsorb over the solid adsorbent bed. The adsorbed oil and grease is then eluted out with an appropriate solvent. The solution is then evaporated and the dry residue of oil and grease is measured by gravimetry. The extraction disks for this analysis are commercially available. Hexane is used as the solvent in this method. The method, however, does not measure the volatile substances that may be present in oil and grease and that boil below 85°C. In addition, compounds insoluble in the hexane cannot be measured.

The sample is acidified to a pH below 2. The SPE disks are conditioned as per the manufacturer's instructions prior to their use. The sample is loaded over the SPE disks. The disks must not become dry before introducing the sample. Maintain an optimum flow rate of 100 mL/min through the disk. The solvent must fully penetrate through the disk. Moderate vacuum may be applied to achieve this flow rate. After the extraction is complete, that is, after all of the sample passes through the disk, apply full vacuum for 10 min to remove as much residual water as possible. Draw a few drops of hexane through the disk by applying slight vacuum. Then, soak the disk for 2 min with hexane. Apply vacuum to cause the hexane to drip through the disk. Collect the eluent in a flask. After the disk dries, repeat the elution with a second portion of the hexane. Pass the combined eluent through 10 g anhydrous Na_2SO_4 placed on a filter paper in a funnel, both rinsed with the solvent, into a clean, tared distilling flask containing boiling chips. Rinse the collection vial and the filter containing Na_2SO_4 with hexane and add to the boiling flask. Heat the flask at 85°C in a water bath. Distill and collect hexane in a receiver cooled at ice bath. After the removal of all the solvent, cool and weigh the flask containing dry residues to constant weight.

$$\text{Oil and grease, mg/L} = \frac{W}{V}$$

where:

W is the weight of residues (mg)

V is the volume of the sample expressed (L)

HYDROCARBONS

Hydrocarbons are all nonpolar substances. Therefore, to measure such hydrocarbons in the sample, all polar constituents of oil and grease are to be removed. The analytical procedure involves removing the polar materials from oil and grease on a polar adsorbent such as silica gel thus leaving behind the nonpolar hydrocarbons in the solvent extract of oil and grease.

The total oil and grease residues obtained from any of the methods outlined above can be used to determine their hydrocarbon contents. The oil and grease residues are then redissolved in 100 mL solvent, either hexane or trichlorotrifluoroethane. An appropriate quantity of silica gel is added into this solution to adsorb all polar substances such as fatty acids. The mixture is then stirred for 5 min on a magnetic stirrer. Filter the solution through a filter paper premoistened with the solvent. Wash the residues with a small portion of solvent. The hydrocarbon portion of the oil and grease left in the solution is then measured by IR spectrometry described above. For gravimetric measurement, the combined filtrate and washings obtained above is transferred into a tared distillation flask and heated on a water bath to distill out the solvent. The dry residue obtained is cooled to ambient temperature and weighed to a constant weight. This residue should consist of all nonpolar hydrocarbons present in the sample. If only the hydrocarbons in the sample are to be measured, the sample is extracted with a suitable immiscible solvent, and the solvent extract treated with silica gel, the solution filtered and analyzed by IR or gravimetric procedure as discussed above.

The amount of silica gel to be added to 100 mL solution of oil and grease for the removal of polar materials depends on the total amount of oil and grease measured in the sample. For every 100 mg of total oil and grease, use 3 g silica gel up to a maximum of 30 g (for 1000 mg total oil and grease). However, if the total oil and grease content is greater than 1000 mg, dilute a smaller portion of the solution (solvent extract) accordingly and adjust the final volume of the solution to 100 mL with the solvent.

SAMPLE COLLECTION AND PRESERVATION

Samples should be collected in wide-mouthed glass bottles with PTFE lined caps. If analysis cannot be performed within 2 h of the sample collection, then acidify the sample to pH below 2 with 1:1 HCl or 1:1 H_2SO_4 and store in a refrigerator.

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42 Oxygen Demand, Biochemical

Biochemical oxygen demand (BOD) is an empirical test that measures the amount of oxygen required for the microbial oxidation of organic compounds in aqueous samples. Such a test measures the amount of oxygen utilized during a specific incubation period (generally, 5 days) for the biochemical oxidation of organic materials and oxidizable inorganic ions, such as Fe^{2+} and sulfide. The incubation is performed in the dark at 20°C ± 1°C. The results of the BOD analyses are used to calculate waste loadings and to design wastewater treatment plants.

Different volumes of sample aliquots are placed in 300 mL incubation bottles and diluted with "seeded" dilution water. The bottles are filled to their full capacity without leaving any headspace, and tightly closed. The BOD bottles are then placed in a thermostatically controlled air incubator or a water bath at 20°C ± 1°C in the dark to prevent any photochemical reaction.

The dilution water is prepared by adding 1–2 mL of phosphate buffer solution to an equal volume of $MgSO_4 \cdot 7\ H_2O$ (22.5 g/L), $FeCl_3 \cdot 6\ H_2O$ (0.25 g/L), and $CaCl_2$ (27.5 g/L) and diluting into the desired volume of reagent grade water. The amount of components per liter of phosphate buffer solution are KH_2PO_4 (8.5 g), K_2HPO_4 (21.75 g), $Na_2HPO_4 \cdot 7\ H_2O$ (33.4 g), and NH_4Cl (1.7 g). The pH of this solution should be 7.2.

Because BOD measures the amount of oxygen needed by the microbes to oxidize the organics in the wastewater, this oxygen must, therefore, be supplied initially into the aqueous medium before incubation. The dilution water, therefore, must contain a sufficient quantity of dissolved oxygen (DO). At ambient conditions, oxygen is slightly soluble in water. Such an amount of oxygen, however, is often sufficient to oxidize trace organics found in relatively clean samples. To ensure availability of surplus oxygen in the medium, the dilution water should be aerated using an air compressor. This enhances the DO concentration.

The concentration of DO before and after incubation is measured. If the microbial population is not sufficiently large in the sample, microorganisms should be added into the dilution water from an outside source. Oxygen consumed by the organics is determined from the difference, and the BOD is calculated as follows:

$$\text{BOD, mg/L} = \frac{(A_1 - A_2)V_2}{V_1}$$

where:

A_1 is the initial concentration DO, mg/L in the dilution water prepared
A_2 is concentration DO, mg/L in the diluted sample after 5 days incubation
V_1 is mL sample aliquot diluted
V_2 is the volume of the BOD bottle, mL

The population of microorganisms should be adequately large to oxidize biodegradable organics. Therefore, the dilution water must be seeded, especially in the BOD determination of such organic-rich polluted water.

Domestic wastewaters, polluted surface waters, or the effluents from biological waste treatment plants are sources of high microbial populations. When such seeded dilution water is used, the BOD is calculated as follows:

$$\text{BOD, mg/L} = \frac{[(A_1 - A_2) - (B_1 - B_2)f] \times V_2}{V_1}$$

where:

B_1 is DO of seed control* before incubation, mg/L

B_2 is DO of seed control after incubation, mg/L

$$f = \frac{\%\ \text{seed in diluted sample}}{\%\ \text{seed in seed control}}$$

GRAPHICAL CALCULATION

BOD may also be calculated by the graphical method (Hach, 2009). These graphical calculations have the following advantages over the single point calculation outlined above:

1. DO of dilution water, even if >0.2 mg/L, would not affect the calculation.
2. The BOD value would be more accurate and reliable because it is based on the valid data points only, while the outlining bad data points are discarded.
3. The initial DO does not need to be measured.

mL Sample Diluted	mg/L DO Remaining
1	8.25
2	7.40
3	6.65
4	5.80
6	3.80
8	1.45

Method

Prepare a series of five or six dilutions using different volumes of sample aliquots. No initial DO is required to be measured. These dilutions are incubated for 5 days. The DO remaining after incubation is measured. A graph is constructed, plotting mL samples diluted versus mg/L DO remaining after incubation. The graph is a straight line over the best-fit points. The slope of the line is equal to the quantity of the DO consumed (as mg/L) per mL of sample. The y-intercept should be equal to the DO in the dilution water after incubation. The BOD is calculated from the following equation:

$$\text{mg/L BOD} = (\text{slope} = V_2) - y\text{-intercept} + \text{sample DO}$$

where V_2 is the volume of the BOD bottle, mL.

The graphical method (Figure 42.1) of BOD calculation is shown in the above table. Sample DO in this example was 3.0 mg/L, determined by potentiometric or Winkler titration. From the above graph (Figure 42.1),

$$\text{slope} = 9/10 = 0.90$$
$$y - \text{intercept} = 9.0\,\text{mg/L}$$
$$\text{If } V_2 = 300\,\text{mL (BOD bottle)}$$
$$\text{Therefore, BOD} = (0.90 \times 300) - 9 + 3$$
$$= 264\,\text{mg/L}$$

* The BOD of the seed is measured like any sample. The seeded dilution water should consume between 0.6 and 1.0 mg/L DO.

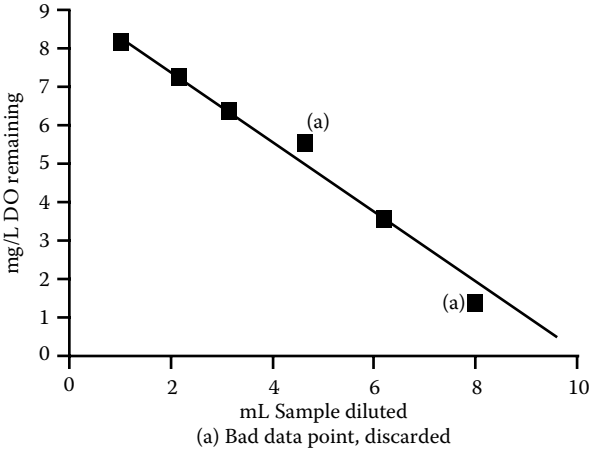

FIGURE 42.1 Example of a graph showing a series of results from an experiment.

MEASUREMENT OF DO

The DO in water may be determined by the following two methods: iodometric titration (Winkler method) and electrode method.

Iodometric or Winkler Method

A measured volume of sample is taken in a glass-stoppered bottle. Add to this a divalent manganese solution ($MnSO_4$). This is followed by the addition of a strong base. This results in the precipitation of the divalent $Mn(OH)_2$, as shown below in the following equation:

$$MNSO_4 + 2NaOH \rightarrow Mn(OH)_2 + Na_2SO_4$$

The DO in the sample rapidly oxidizes an equivalent amount of dispersed Mn^{2+} precipitate to the higher-valent manganese (IV) oxide hydroxide flocculent, which has the formula $MnO(OH)_2$. This is shown below in the following equation:

$$2Mn^{2+} + O_2 + 4OH^- \rightarrow 2MnO(OH)_2$$

In the presence of iodide ion, and in acid medium, Mn^{4+} is reduced back to divalent Mn^{2+}, thus liberating I_2.

$$Mn^{4+} + 2I^- \xrightarrow{\text{acid}} Mn^{2+} + I_2$$

The iodine liberated is stoichiometrically equivalent to the DO in the sample. It is titrated against a standard solution of $Na_2S_2O_3$ or phenyl arsine oxide using starch indicator to a colorless end point.

$$\text{mg DO/L} = \frac{A \times N}{\text{mL sample}} \times 8000$$

where:

A is the mL of the titrants, $Na_2S_2O_3$ or PAO
N is the normality of the titrant

In the BOD measurement, the sample volume is usually 300 mL. The milliequivalent weight for oxygen is 8000.

Various modifications of the original Winkler method have been developed to eliminate interferences. This includes adding azide to suppress any interference from the NO_2^- in the sample.

In this method, the sodium azide solution is added before the acidification into the sample mixture containing Mn^{4+} flocculent. Azide prevents any possible reaction of nitrite with iodide. Interference from Fe^{3+} is overcome by adding a small amount of KF solution (1 mL of 40% solution) before the acidification.

If the normality of the $Na_2S_2O_3$ titrant is 0.0375 N, each mL of titrant is equivalent to 1 mg of DO, when the entire 300 mL content of the BOD bottle is titrated.

Electrode Method

Oxygen-sensitive membrane electrodes are commercially available. The electrode in such a system is covered with an oxygen-permeable plastic membrane, thus protecting it from impurities. The current is proportional to the activity of the dissolved molecular oxygen, and at low concentration, to the amount of DO. Before the measurement of DO in the sample, calibrate the electrodes using standards of known DO concentrations (determined from iodometric titrations).

KINETICS OF BOD REACTION

The BOD reaction follows first-order kinetics. The reaction rate is proportional to the amount of oxidizable organic matter remaining at any time. In addition, the reaction rate depends on the temperature. The population of microorganisms should be adequately large and stabilized. The BOD value for any incubation period may be theoretically determined from its ultimate BOD and the rate constant for the reaction from the following equation:

$$Bt = U(1-10^{-kt})$$

where:

Bt is the BOD-t for t days of incubation period
U is the ultimate BOD
k is the rate constant for the reaction

In order to calculate the BOD at any time, the k value must be experimentally determined. For this, the DO concentrations should be measured for any two incubation periods and then calculated from the following equation for the first-order reaction:

$$k = \frac{\ln\left(\frac{c_1}{c_2}\right)}{T_2 - T_1}$$

where:

c_1 is the concentration of DO, mg/L after T_1 incubation time
c_2 is the concentration of DO, mg/L after T_2 incubation period
k is the rate constant for the reaction

Because the ultimate BOD should be theoretically equal to the COD, the BOD at any time may also be approximately estimated from the COD value. This is shown in the following example.

EXAMPLE 42.1

Two aliquots of a sample were diluted equally and the DO contents were measured after 2 and 5 days incubation periods, respectively. The DO concentrations were 6.5 and 4.3 mg/L, respectively. Determine the rate constant k for the BOD reaction.

$$k = \frac{\ln\left(\frac{6.5\,\text{mg/L}}{4.3\,\text{mg/L}}\right)}{(5-2)\text{days}}$$
$$= 0.137$$

From the known k value, the BOD may be calculated for any incubation period. However, to solve this problem, the ultimate BOD or the BOD for any other incubation period must be known. This is illustrated in the following problem.

EXAMPLE 42.2

The ultimate BOD of a sample was measured as 540 mg/L after a 30-day incubation period. Determine the BOD-5, if the rate constant, k, is 0.05 for the reaction.

$$\text{BOD} = 540(1-e^{-0.005\times5})\text{mg O}_2\text{/L}$$
$$= 540(1-0.78)\text{mg O}_2\text{/L}$$
$$= 119\,\text{mg/L}$$

Alternatively, the DO concentration after the 5-day incubation may be theoretically calculated from the DO concentration measured after the 30-day incubation. Such calculation requires the use of the first-order rate equation. From the initial DO before incubation that was measured and the DO for a 5-day incubation that may be theoretically estimated, the BOD-5 may be determined. However, for any such calculations, the rate constant, k, must be known.

REFERENCE

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Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

43 Oxygen Demand, Chemical

Chemical oxygen demand (COD) is a measure of the oxygen equivalent of organic matter in the sample that is susceptible to oxidation by a strong oxidizing agent. A boiling mixture of potassium dichromate ($K_2Cr_2O_7$)–H_2SO_4 can oxidize most types of organic matter and it is generally used in COD determination. Other strong oxidants, such as $KMnO_4$–H_2SO_4, are also effective.

The complete oxidation of organic compounds under such strong oxidizing conditions produces carbon dioxide and water. Other additional products such as HCl or NO_2 may, however, form if the organic compound contains a Cl or N atom, respectively, in its molecule. The COD for any organic compound or any oxidizable inorganic ion (i.e., anions or metal ions in their lower oxidation states) can be theoretically calculated from writing a balanced equation. Some oxidation reactions are presented below and the methods for calculating COD are shown in the following problem:

$$2C_5H_{10} + 15O_2 \xrightarrow[\text{Acid}]{K_2Cr_2O_7} 10CO_2 + 10H_2O$$

(2 mol *n*-pentane reacts with 15 mol O_2)

$$C_2H_5OH + 3O_2 \xrightarrow[\text{Acid}]{K_2Cr_2O_7} 2CO_2 + 3H_2O$$

(1 mol ethanol reacts with 3 mol O_2)

$$2Fe^{2+} + O_2 \xrightarrow[\text{Acid}]{K_2Cr_2O_7} 2Fe^{3+} + 2O^-$$

(Metal ion is oxidized to higher oxidation state.)

PROBLEM 43.1

A 250 mL aliquot of wastewater containing 72 mg/L of *n*-propanol (C_3H_7OH) was spiked with 50 mL of 100 mg/L acetone solution. Determine the COD as mg/L of the resulting solution.

To solve this problem, first we write the balanced oxidation reactions for propanol and acetone, which are as follows:

$$2C_3H_7OH + 9O_2 \rightarrow 6CO_2 + 8H_2O$$

(*n*-Propanol)

$$CH_3COCH_3 + 4O_2 \rightarrow 3CO_2 + 3H_2O$$

(Acetone)

$$250\,\text{mL of } 72\,\text{mg/L } n\text{-propanol} = 0.25\,\text{L} \times \frac{72\,\text{mg}}{\text{L}} \times 18\,\text{mg } n\text{-propanol}$$

The oxygen requirement for this 18 mg *n*-propanol

$$= 0.018\,\text{g } C_3H_7OH \times \frac{1\,\text{mol } C_3H_7OH}{60\,\text{g } C_3H_7OH} \times \frac{9\,\text{mol } O_2}{2\,\text{mol } C_3H_7OH} \times \frac{32\,\text{g } O_2}{1\,\text{mol } O_2}$$

$$= 0.0432\,\text{g } O_2$$

or 43.2 mg O_2. Similarly,

$$50\,\text{mL of } 100\,\text{mg/L acetone} = 0.05\,\text{L} \times \frac{100\,\text{mg}}{\text{L}}$$

or 5 mg acetone, the oxygen requirement for which

$$= 0.005\,\text{g acetone} \times \frac{1\,\text{mol acetone}}{58\,\text{g acetone}} \times \frac{4\ \text{mol } O_2}{1\,\text{mol acetone}} \times \frac{32\,\text{g } O_2}{1\,\text{mol } O_2}$$
$$= 0.0011\,\text{g } O_2 \text{ or } 11.0\,\text{mg } O_2$$

Thus, the total amount of O_2 required to oxidize 18 mg *n*-propanol and 5 mg acetone = 43.2 mg O_2 + 11.0 mg O_2 = 54.2 mg O_2.

The total volume of sample + spiking solution = 250 + 50 mL = 300 mL, that is, 54.2 mg O_2/300 mL solution, or

$$\frac{54.2\,\text{mg } O_2}{300\,\text{mL}} \times \frac{1000\,\text{mL}}{1\,\text{L}} = 180.7\,\text{mg } O_2/\text{L}$$

Therefore, the COD of the resulting solution = 180.7 mg/L.

Certain inorganic substances also contribute to the COD. These include oxidizable anions such as S^{2-}, SO_3^{2-}, NO_2^-, PO_3^{3-}, AsO_2^-, ClO^-, ClO_2^-, ClO_3^-, BrO_3^-, IO_3^-, and SeO_3^{2-} and such metal ions as Fe^{2+}, Cu^{1+}, Co^{2+}, Sn^{2+}, Mn^{2+}, Hg^{1+}, and Cr^{3+} (mostly transition metal ions in their lower oxidation states). If any of these ions is present in detectable concentration, its COD can be calculated from the balanced equation

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$$

Thus, 1 mol of nitrite ion (NO_2^- would react with 0.5 mol of O_2 to form nitrate (NO_3^-), that is, 46 g NO_2^- would require 16 g oxygen; or the COD due to 1 mg/L NO_2^- would be 0.35 mg/L. This is equivalent to a COD of 1.15 mg/L for every 1 mg/L of nitrite nitrogen (NO_2^-—N).

Ammonia present in the sample also contributes to the COD. However, in the presence of excess free Cl^-, it is converted into HH_4Cl and is not oxidized. Long-chain aliphatic compounds are often difficult to oxidize. A catalyst, Ag_2SO_4, is therefore added to promote such oxidation. Halide ions present in the sample may, however, react with Ag_2SO_4 forming silver halide. Such halide interference may be partially overcome by adding $HgSO_4$.

An aliquot of sample is refluxed in a strong acid solution of a known excess of potassium dichromate ($K_2Cr_2O_7$) in the presence of Ag_2SO_4 and $HgSO_4$. Cr^{6+} (dichromate ion) is reduced to Cr^{3+} during oxidation. The net ionic reaction in the acid medium is as follows:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O$$

After the digestion is completed, the amount of Cr^{6+} consumed is determined either by titration or by colorimetry. The initial amount of Cr^{6+}, and that which is left after the reaction, are determined by titrating against a standard solution of ferrous ammonium sulfate (FAS) using ferroin indicator. The initial amount of Cr^{6+} may also be calculated from the standard grade of $K_2Cr_2O_7$ used to prepare the solution.

The reaction of FAS with Cr^{6+} is as follows:

$$3Fe^{2+} + Cr^{6+} \rightarrow 3Fe^{3+} + Cr^{3+}$$

1,10-Phenanthroline (ferroin), which is used as an indicator in this titration, forms an intense red color with Fe^{2+}, but no color with Fe^{3+}. When all the Cr^{6+} is reduced to Cr^{3+}, Fe^{2+} reacts with the indicator forming the ferroin complex. The color of the solution changes from greenish blue to reddish brown signaling the end point of titration.

The COD in the sample is calculated as follows:

$$\text{COD, mg/L} = \frac{(A-B)\times \text{N}\times 8000}{\text{mL Sample}}$$

where:

A is the mL FAS required for the titration of the blank
B is the mL FAS required for the titration of the sample
N is the normality of FAS

The multiplication factor 8000 is derived as follows.

As we see from the reaction above, 3 mol of Fe^{2+} require 1 mol of Cr^{6+}, that is, 0.333 mol $K_2Cr_2O_7$/each mol FAS titrant. In addition, we used 0.0417 mol $K_2Cr_2O_7$. Multiplying by 1000 to convert grams to milligrams, we finally get a factor of 0.333 × 1000/0.0417 or 8000.

STANDARDIZATION OF FAS TITRANT

98 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water + 20 mL concentrated H_2SO_4 and dilute to 1 L. This solution of approximately 0.25 M (or 0.25 N) strength is titrated against the standard solution of $K_2Cr_2O_7$. The latter solution is made by dissolving 12.259 g $K_2Cr_2O_7$ (dried at 105°C for 2 h) in distilled water and diluting to 1 L. This solution has a strength of 0.0417 M or a normality of 0.25 N. (The equivalent weight of $K_2Cr_2O_7$ = 294.22 (Formula weight)/6 or 49.036.)

$$\text{Normality of FAS} = \frac{\text{mL } K_2Cr_2O_7 \times 0.25}{\text{mL FAS}}$$

Indicator Solution

- Dissolve 1.485 g 1,10-phenanthroline monohydrate and 0.695 g $FeSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 L.
- Ag_2SO_4: 5.5 g is dissolved in 1000 g of concentrated H_2SO_4.

SAMPLE TREATMENT

To a 50 mL sample in a 500 mL refluxing flask, 1 g $HgSO_4$ is added. This is followed by the slow addition of 5 mL of concentrated H_2SO_4 (containing Ag_2SO_4), some glass beads, a 25 mL 0.0417 M $K_2Cr_2O_7$, and 70 mL of concentrated H_2SO_4 slowly. The mixture is refluxed for 2 h, cooled, diluted, and titrated against standard FAS.

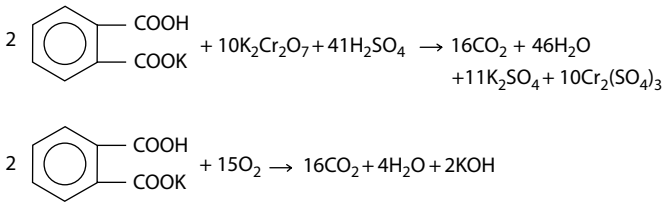
For samples containing low organics, $K_2Cr_2O_7$ solution of 0.00417 M strength should be used. This may be titrated against 0.025 N FAS. The sample digestion may be performed under open reflux conditions as described earlier, or in borosilicate ampules heated at 150°C on a heating block.

When such culture tubes or ampules are used, sample volumes must be below 10 mL and the acid and $K_2Cr_2O_7$ solutions must be in small volumes accordingly. The total volume of sample plus reagents should not exceed two-thirds of the volume of the container.

COLORIMETRIC ANALYSIS

Colorimetric measurement of COD is faster and easier to perform than the titrimetric analysis. In addition, additional reagents are not required. The sample is digested in an ampule, culture tube, or vial under closed reflux conditions. The concentration of dichromate is determined from its absorbance, which is measured by a spectrophotometer set at 600 nm and compared against the standard calibration curve. Hach COD vials (Hach Company, Lovedale, Co.) are commercially available for COD measurements in low, medium, and high ranges. For low range COD analysis, the Hach method measures the amount of yellow Cr^{6+} left after the dichromate reduction. On the other hand, high range measurement determines the amount of green Cr^{3+} produced.

KHP is used as a reference standard for COD analysis. The theoretical COD for 1 mg KHP is 1.175 mg, which is determined from either of the following equations:



As noted in the first equation, the oxidizing agent $K_2Cr_2O_7$ provides all the oxygen required for the oxidation of the organic material in a closed system.

44 Oxyhalides

Oxyhalides refer to anions containing one halogen atom and one or more oxygen atom(s) with a single negative charge and include perchlorate (ClO_4^-), chlorate (ClO_3^-), chlorite (ClO_2^-), and hypochlorite (ClO^-) and similar oxo anions of bromine and iodine, such as perbromate (BrO_4^-), bromate (BrO_3^-), or iodate (IO_4^-). Fluorine, however, does not form such oxyfluoride anions. A few oxyhalide anions, especially, the disinfection by-products, perchlorate, chlorate, chlorite, and bromate are found in ground- and surface-water in the United States. Perchlorate salts are used in rocket propellants and explosives. Chlorine dioxide, ClO_2, and hypochlorite salts of sodium and calcium are used in water treatment to kill bacteria. Oxyhalides are strong oxidizing agents. Perchlorate and other oxyhalide anions are suspected carcinogens and are globally regulated. The U.S. EPA has promulgated analytical methods to measure oxyhalides that are well below their maximum contaminant levels in drinking water for compliance monitoring.

ANALYSIS OF OXYHALIDES BY U.S. EPA METHODS

Oxyhalides in water are best analyzed by ion chromatography. The U.S. EPA Methods 300.1, 317.0, 321.0, and 326.0 are all based on ion chromatography (U.S. EPA. 1997, 2001). These methods do not differ much from each other. Two such methods are briefly outlined below.

U.S. EPA Method 300.1

This method may be used to measure the oxyhalide anions, chlorate, bromate, and chlorite along with six other inorganic anions, namely, bromide, chloride, nitrite, nitrate, orthophosphate, and sulfate. Although not mentioned in this method, the same procedure should be applicable to measure other oxo-halide anions, such as perchlorate in water. An ion chromatograph, such as Dionex DX500 or equivalent may be used for analysis. Follow the manufacturer's instruction manual for the operation of the instrument. The standard conditions are given below. Other columns, chromatographic conditions, or detectors may be used if quality control requirements are met.

Anion separator column: Dionex AS9-HC, 2 mm or equivalent
Anion guard column: Dionex AS9-HC, 2 mm or equivalent
Detector: Suppressed Conductivity Detector, Dionex CD20 or equivalent
Suppressor: ASRS-I, external source electrolytic mode, 100 mA current
Eluent: 0.009 M Na_2CO_3
Sample loop: 10 μL
System backpressure: 2800 psi
Background conductivity: 22 uS
Total analysis time (recommended): 25 min

The sample is filtered through a 0.45 μL particulate filter. Using an injection loop introduce 50 μL sample into a 2 mm column or 200 μL into a 4 mm column. Sodium carbonate solution at 9.0 mM concentration is used as the eluent in the analysis. Such eluent solution may be prepared by dissolving 1.1 g Na_2CO_3 [497-19-8] in 2 L reagent water. Dichloroacetate may be used as the surrogate in the analysis. This surrogate solution is prepared by dissolving 0.065 g potassium dichloroacetate, $Cl_2CHCOOK$ [1559-59-2] in reagent water to a volume of 100 mL to give a concentration of 0.50 mg/mL. An appropriate volume of this surrogate standard solution is spiked into the sample

to give a concentration of 1 mg/L in the sample. The surrogate solutions should be prepared fresh and must be used within 3 months. The surrogate recoveries must fall within 90%–115% for proper instrument performance and as acceptance criteria of analytical data. The anions are identified from the retention times of their peaks in the ion chromatogram and quantified against the area response in their calibration standards. The standard solutions of oxyhalide anions for calibration may be purchased as certified solutions or made from their stock standard solutions as follows. The prepared oxyhalide standards should be preserved in ethylenediamine solution.

Chlorate, ClO_3^- (1000 mg/L): dissolve 0.1275 g sodium chlorate, $NaClO_3$ [7775-09-9] in reagent grade water and dilute the solution to 100 mL.

Chlorite, ClO_2^- (1000 mg/L): dissolve 0.1676 g 80% technical grade $NaClO_2$ [7758-19-2] in reagent grade water and dilute to 100 mL. An iodometric titration should be performed to determine the exact strength of the $NaClO_2$ in the 80% technical grade material.

Bromate, BrO_3^- (1000 mg/L): dissolve 0.1180 g sodium bromate, $NaBrO_3$ [7789-38-0] in reagent grade water and dilute the solution to 100 mL.

Ethylenediamine preservation solution (100 mg/L): dilute 2.8 mL of ethylenediamine (99%) [107-15-3] to 25 mL with reagent water. This solution should be prepared fresh every month. This preservation solution should be added to the sample such that its final concentration in the sample is 50 mg/L.

U.S. EPA Method 317.0

This method is also based on ion chromatography and in a way may be termed as an extension of the U.S. EPA Method 300.0 outlined above. While in Method 300.0 all anions of interest including bromate (BrO_3^-) are measured with a conductivity detector, in the Method 317.0 bromate is measured with an UV/VIS absorbance detector. Thus, after the analysis of common ions by a conductivity detector, the sample is treated with a postcolumn reagent, *o*-anisidine (3,3′-dimethoxybenzidine dihydrochloride) for measuring bromate with an UV/VIS absorbance detector. The analytical system consists of an ion chromatographic pump and all required accessories including syringes, analytical columns, compressed gasses, suppressor, conductivity detector, mixing "tee," postcolumn reagent delivery system, reaction coil, reaction coil heater, and a UV/VIS absorbance detector. The instrument is attached to a PC-based data acquisition and control system. A volume of 225 μL aqueous sample is introduced using a loop into the ion chromatograph. The detection limit for measuring bromate by this method is lower than that obtained from using Method 300.0. It may be quantified in the concentration range 0.5–15 μg/L in the postcolumn system.

Preparation of postcolumn reagent for bromate analysis: to 300 mL reagent grade water in a 500 mL volumetric flask, add 40 mL of 70% nitric acid (>99.99% purity). Into this solution, add 2.5 g of KBr (reagent grade). To this mixture, add a solution of *o*-dianisidine dihydrochloride in methanol (250 mg dissolved in 100 mL methanol). The solution mixture is diluted to 500 mL with reagent water.

Interference

The presence of chlorite can interfere in the quantitation of low concentration of bromate on the postcolumn UV/VIS absorbance detector. Residual chlorine dioxide, ClO_2 is often found in water from treatment plants. The presence of such ClO_2 in the sample can result in formation of additional chlorite ion. Therefore, if such residual chlorine dioxide is known or suspected to be present in the sample, it should be purged out by bubbling the sample for about 5 min with an inert gas such as helium, argon, or nitrogen at the time of sample collection and before adding ethylenediamine preservation. Chlorite must be removed before analyzing bromate. It is done by treating the sample with ferrous sulfate, $FeSO_4$, a reducing agent. The preserved sample is acidified to a pH of 5–6 and $FeSO_4$ is added to it. The sample is allowed to stand for about 10 min. Insoluble ferric hydroxide,

$Fe(OH)_3$ formed is filtered using a 0.45 micron membrane and excess of iron is removed by passing the filtered sample through a solid phase extraction cleanup cartridge in H^+ form.

Sample Collection, Preservation, and Storage

Samples should be collected in glass or plastic bottles and preserved with ethylenediamine solution (50 mg added to 1 L of sample). For chlorite analysis, the bottle should be opaque or amber to protect from light. Samples must be refrigerated below 6°C and stored no more than 28 days for all oxyhalide ions except chlorite. The holding time for chlorite is 14 days.

Quality Control

The quality control requirements include an initial laboratory demonstration capability and after that, subsequently analyzing a laboratory reagent blank and running calibration check standards and instrument performance-check solutions in each analysis batch. The chromatographic performance should be assessed from the peak symmetry and also from monitoring the retention time drift in the surrogate peak over time. Peak symmetry may be calculated as the peak Gaussian factor (PGF) from the following formula:

$$\mathrm{PGF} = 1.83 \times W_{1/2} / W_{1/10}$$

where $W_{1/2}$ and $W_{1/10}$ are peak width at half and 1/10th of height, respectively.

Other major components of quality control requirements should include running a duplicate analysis in each batch of samples to determine the precision of analysis and measuring the accuracy from the recovery of the known amount of analytes added into the sample.

MISCELLANEOUS METHODS

Several methods to measure trace concentrations of oxyhalide anions in aqueous phase have been reported. Most of these methods, however, are based on the ion chromatography technique. Liu et al. (2002) have described a procedure to measure bromate, perchlorate, iodate, and chlorate in drinking water by ion chromatography. The method involves removal of any superfluous chloride first using OnGuard Ag cartridge and then carrying out sample concentration in a microwave oven. The detection limits of these ions have been reported to be in the range 0.10–0.21 μg/L. Medina et al. (2005) have investigated the use of solid-phase extraction cartridges as an alternative to large volume injection loops to achieve low level quantitation (microgram/liter level) of perchlorate ion. Such cartridges are commercially available. A volume of 100–1000 mL water sample is filtered through a strong anion exchange cartridge that removes perchlorate from the solution by anion exchange. The perchlorate is then extracted with 4 mL of 1% NaOH solution. Competing anions such as chloride, sulfate, and carbonate may be removed by a cleanup step. Perchlorate is detected using an ion chromatograph. An MDL of 0.82 μg/L was reported for 1 L water sample at 2 μg/L perchlorate concentration.

Oxyhalide anions can also be analyzed by other techniques such as using a liquid chromatography-tandem triple-quadrupole mass spectrometry (LC–MS/MS) system. The LC–MS/MS system is also simple and rapid and can simultaneously measure several anions including oxyhalides. Snyder et al. (2005) have described a method to measure bromate, chlorate, iodate, and perchlorate in water at concentration levels below 1 μg/L. A volume of 10 mL aqueous sample is first passed through barium and hydronium cartridges, respectively, to remove sulfate and carbonate ions from the sample. After this, 10 μL of sample is injected directly into the LC–MS/MS system. The analytes are ionized under electrospray ionization in negative mode. The MDLs reported in this method for these anions are 0.021 μg/L for perchlorate, 0.045 μg/L for bromate, 0.070 μg/L for iodate, and 0.045 μg/L for chlorate.

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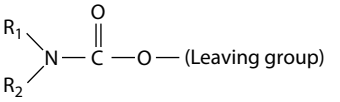
45 Pesticides
Carbamate, Urea, and Triazine

A large number of nitrogen-containing pesticides are characterized by the carbamate or urea functional group or triazine ring in their structures. These substances constitute the three most common classes of nitrogen-containing pesticides. The structural features of these three distinct classes of substances are shown below:

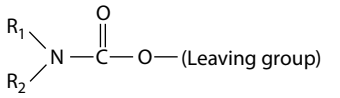


Carbamate

where R_1 and R_2 are alkyl or aryl groups or hydrogen atoms. Compounds containing a methyl group attached to the N atom are also known as N-methyl carbamates.

The substitution of one or both of the oxygen atoms with sulfur in the above structure gives thiocarbamate.

The structure of the urea-type pesticide is similar to carbamate, except that a nitrogen atom replaces the terminal oxygen atom.



Urea type

Triazine is a nitrogen heterocyclic ring containing three N atoms in the ring.

Triazine

Discussed below are some pesticides that fall under the above structural features. Compounds having the same type or closely related structures can be analyzed by the same methodologies. Certain instrumental techniques such as GC, GC/MS, or HPLC can be applied in general to analyze these substances irrespective of their structures. For example, using a capillary column of appropriate polarity and a NPD in N-specific mode, many types of nitrogen-containing pesticides can be analyzed. Only the pesticides of carbamate, urea, and triazine types are presented in this chapter. This chapter includes many pesticides that have not yet been added in the U.S. EPA priority pollutant list. Refer to Section III of this book for the analysis of individual substances including those that are not discussed here.

CARBAMATE PESTICIDES

Carbamate pesticides are best analyzed by HPLC using postcolumn derivatization technique. Some common carbamate pesticides are listed in Table 45.1. Compounds are separated on a C-18 analytical column and then hydrolyzed with 0.05 N sodium hydroxide. Hydrolysis converts the carbamates

TABLE 45.1
Some Common Carbamate Pesticides

CAS No.	Pesticides	Alternate Names(s)
[116-06-3]	Aldicarb	Temik
[1646-88-4]	Aldicarb sulfone	Aldoxycarb, Standak
[1646-87-3]	Aldicarb sulfoxide	—
[671-04-5]	Banol	Carbanolate
[101-21-3]	Chlorpropham	Chloro IPC
[63-25-2]	Carbaryl	Sevin, Arylam
[1563-66-2]	Carbofuran	Furadan
[17804-35-2]	Benomyl	Benlate
[2032-59-9]	Aminocarb	Matacil
[22781-23-3]	Bendiocarb	Ficam
[2032-65-7]	Methiocarb	Mercaptodimethur, Mesurol
[16752-77-5]	Methomyl	Lannate
[23135-22-0]	Oxamyl	—
[23135-22-0]	Pirimicarb	Pirimor
[2631-37-0]	Promecarb	Carbamult
[122-42-9]	Propham	IPC
[114-26-1]	Propoxur	Baygon, Aprocarb
[1918-18-9]	Swep	—
[3766-81-2]	Fenobucarb	Baycarb
[1918-11-2]	Terbucarb	Terbutol
[6988-21-2]	Dioxacarb	Elocron

to their methylamines that are then reacted with *o*-phthalaldehyde and 2-mercaptoethanol to form highly fluorescent derivatives. A fluorescence detector detects the derivatives. *o*-Phthalaldehyde reaction solution is prepared by mixing a 10 mL aliquot of 1% *o*-phthalaldehyde solution in methanol to 10 mL of acetonitrile containing 100 μL of 2-mercaptoethanol and then diluting to 1 L with 0.05 N sodium borate solution.

The following conditions are recommended for liquid chromatography (LC), fluorometric detection, and for postcolumn hydrolysis and derivatization.

LC Columns

C-18 reverse phase HPLC column, for example, 25 cm × 4.6 mm stainless steel packed with 5 μm Beckman Ultrasphere, or 15 cm × 2.9 mm stainless steel packed with 4 μm Nova Pac C18, or 25 cm × 4.6 mm stainless steel packed with 5 μm Supelco LC-1 or equivalent.

Chromatographic Conditions

- Solvent A—reagent grade water acidified with phosphoric acid (10 drops/1 L)
- Solvent B—methanol/acetonitrile (1:1)
- Flow rate—1 mL/min

Hydrolysis Conditions

- Solution: 0.05 N NaOH
- Flow rate: 0.7 mL/min
- Temperature: 95°C
- Residence time: 35 s

Postcolumn Derivatization Conditions

- Solution: *o*-phthalaldehyde/2-mercaptoethanol
- Flow rate: 0.7 mL/min
- Temperature: 40°C
- Residence time: 25 s

Fluorometer Conditions

- Excitation wavelength: 330 nm
- Emission wavelength: 418 nm cutoff filter

Extraction

Aqueous samples, especially those that are clean, may be directly injected into the reverse phase HPLC column. No extraction is required for this. A 200–400 μL aliquot of the sample may be injected. Wastewater, aqueous industrial waste, and leachates can be extracted with methylene chloride. Nonaqueous samples such as soils, sediments, solid wastes, sludge, oils, and nonaqueous liquids are extracted with acetonitrile. Solids and sludge are dried at 105°C and an accurately weighted dried sample is repeatedly extracted with acetonitrile. The mixture should be shaken at least for an hour using a platform shaker. Oils and oily wastes should be extracted with a mixture of hexane and acetonitrile for several hours. Transfer the solvents into a separatory funnel. Shake for a few minutes and then allow the solvent phases to separate. Collect the acetonitrile layer containing the carbamates in a volumetric flask. Discard the hexane phase.

For dirty and heavily contaminated samples, cleanup of the extracts may often become necessary. This is done by treating with 20 mL of ethylene glycol and evaporating the solvent in a water bath, at 50°C–60°C in a stream of nitrogen. The ethylene glycol residue is then combined with a few mL of methanol, and the mixture is then passed through a prewashed C-18 reverse phase cartridge. Analytes that are now adsorbed on the cartridge are eluted with methanol for HPLC analysis.

Solvent exchange is very crucial for HPLC analysis. The methylene chloride or acetonitrile extract is exchanged into methanol as described above, using ethylene glycol before passing through any C-18 reverse phase cartridge.

Certain substances, such as alkyl amines, produce fluorescence. The presence of such fluorescence compounds in the sample can produce positive interference. Base hydrolysis may result in the formation of such substances. Similarly, coeluting compounds that quench fluorescence may cause negative interference. Blanks should be run using organic-free reagent water without sodium hydroxide and *o*-phthalaldehyde to determine the presence of such interfering substances.

Air analysis for carbamate pesticides may be performed by sampling air over 1 μm PTFE membrane. The analytes collected over the membrane are extracted with methylene chloride, exchanged into methanol, and analyzed by HPLC using the postcolumn derivatization technique as described above. Certain pesticides may also be analyzed by the colorimetric method (see Section III under selected individual compounds).

UREA PESTICIDES

Urea pesticides are structurally similar to carbamates. Some common pesticides of this class are listed in Table 45.2. These substances can be determined by the reverse phase HPLC method. Aqueous samples can be analyzed by U.S. EPA Method 553 using a reverse phase HPLC column interfaced to a mass spectrometer with a particle beam interface. The outline of the method is described below.

TABLE 45.2
Some Common Pesticides Containing Urea Functional Group

CAS No.	Pesticides	Alternate Name(s)
[13360-45-7]	Chlorbromuron[a]	Maloran
[1982-47-4]	Chloroxuron[a]	Tenoran
[330-54-1]	Diuron[a]	Karmex
[101-42-8]	Fenuron	Dybar
[4482-55-7]	Fenuron TCA[a]	Urab
[2164-17-2]	Fluometuron[a]	Cotoran
[34123-59-6]	Isoproturon	Arelon
[330-55-2]	Linuron[a]	Lorox
[3060-89-7]	Metobromuron[a]	Patoran
[150-68-5]	Monuron[a]	Telvar
[140-41-0]	Monuron TCA[a]	Urox
[555-37-3]	Neburon[a]	Kloben
[66063-05-6]	Pencycuron[a]	Monceren
[1982-49-6]	Siduron	Tupersan
[34014-18-1]	Tebuthiuron	EL-103

[a] Contains halogen atoms in the molecules.

Aqueous samples are extracted by LLE with methylene chloride. The sample extract is concentrated by evaporating methylene chloride and exchanging the solvent to methanol. Alternatively, the sample may be extracted by SPE, using a sorbent cartridge packed with C-18 impregnated on silica or a neutral polystyrene/divinylbenzene polymer. The sample is mixed with ammonium acetate (0.8 g/L) prior to extraction. The cartridge is flushed with methanol and then the sample is passed through the cartridge. The analytes are eluted from the cartridge with methanol and concentrated by evaporation. The samples should be extracted within 7 days. The extracts must be stored below 0°C and analyzed within 3 weeks.

The sample extract is injected into a HPLC containing a reverse phase HPLC column. The analytes are identified by comparing their retention times with that of the standard. A more reliable and confirmatory test is to use a mass spectrometer equipped with a particle beam and interfaced to the HPLC column. The compounds are identified from their mass spectra as well as retention times. The chromatographic column and conditions are described below.

Column

- C-18 Novapak (Waters) or equivalent, packed with silica, chemically bonded with octadecyldimethylsilyl groups.
- Condition the column by pumping acetonitrile through it for several hours at a rate of 1–2 drops/min.

Liquid Chromatograph

LC should be able to maintain flow rates between 0.20 and 0.40 mL/min and perform a gradient elution from 100% solvent A (75:25 v/v water:acetonitrile containing 0.01 ammonium acetate) to solvent B (acetonitrile).

Use an additional LC pump for postcolumn addition of acetonitrile at a constant rate (0.1–0.5 mL/min).

TABLE 45.3
DFTPPO Tuning Criteria for LC/MS System Performance Check

Mass *m/z*	Ion Abundance Criteria
77	Major ion, must be present
168	Major ion, must be present
169	4%–10% of mass 168
271	Major ion, base peak
365	5%–10% of base peak
438	Must be present
458	Molecular ion, must be present
459	15%–24% of mass 458

Mass Spectrometer

Electron ionization must occur at a nominal electron energy of 70 eV. Scan range 45–500 amu with 1–2 s/scan. The MS should be tuned using a performance check solution of DFTPPO. The latter is obtained by adding a slight excess of H_2O_2 to a solution of DFTPP. The product crystals are washed and dissolved in acetonitrile to prepare a 100 ppm solution. Inject 400–500 ng DFTPPO into the LC/MS to measure ion abundance criteria for the system performance check, especially to check mass measuring accuracy and the resolution efficiency. The DFTPPO tuning criteria is given in Table 45.3.

The particle beam LC/MS interface must reduce the system pressure to about 1×10^{-6} to 1×10^{-4} Torr at which electron ionization occurs.

Precision and Accuracy

The precision and accuracy data are not available for all the urea pesticides listed in Table 45.3. However, a matrix spike recovery between 70% and 130% and a RSD below 30% should be achieved for aqueous samples. Samples should be spiked with one or more surrogates. Compounds recommended as surrogates are benzidine-d_8, 3,3-dichlorobenzidine-d_6, and caffeine-$^{15}N_2$. Surrogate concentrations in samples or blank should be 50–100 μg/L.

TRIAZINE PESTICIDES

Triazine pesticides (herbicides) can be determined primarily by all the major instrumental techniques: HPLC, GC, and GC/MS, following sample extraction. Detection limits in low ppb range can be achieved using GC-NPD in the nitrogen-specific mode. HPLC method using UV detection (254 nm) may be alternatively employed if such a low range of detection is not required. Analytes may alternatively be determined by GC-FID or GC/MS. A polyphenylmethylsiloxane capillary column (30 m length, 0.25 mm ID, and 0.25 μm film thickness) having intermediate polarity, such as DB-35, AT-35, SPB-35, Rtx-35, or equivalent, or a polycyanopropylphenylmethylsiloxane column such as OV-1701, DB-1701, AT-1701, SPB-7, or equivalent, can provide adequate resolution of triazines for GC or GC/MS analysis. Some common triazine pesticides are listed in Table 45.4.

Conditions for typical HPLC analysis are given below:

Column: Accubond ODS (C-18) (15 cm × 4.6 mm ID × 5 μm film thickness)
Mobile phase: Acetonitrile/0.01 M K_2HPO_4 (35:65)
Flow rate: 1.5 mL/min
Detector: UV at 254 nm

TABLE 45.4
Some Common Triazine Pesticides

CAS No.	Pesticides	Alternate Names(s)
[834-12-8]	Ametryne	Gesapax
[101-05-3]	Anilazine	Kemate, Dyrene
[1610-17-9]	Atraton	Gestamin
[1912-24-9]	Atrazine	Atratol, Gesaprim
[64902-72-3]	Chlorsulfuron	Glean
[21725-46-2]	Cyanazone	Bladex
[4147-51-7]	Dipropetryne	Sancap
[21087-64-9]	Metribuzin	Sencor, Lexone
[32889-48-8]	Procyazine	Cycle
[1610-18-0]	Prometon	Primatol
[7287-19-6]	Prometryne	Caparol
[139-40-2]	Propazine	Gesamil, Milogard
[122-34-9]	Simazine	Amizine, Gesapun
[1014-70-6]	Simetryne	Gybon
[5915-41-3]	Terbuthylazine	Gardoprim
[886-50-0]	Terbutryne	Prebane
[64529-56-2]	Tycor	Ethiozin, Ebuzin
[51235-04-2]	Velpar	Hexazinone

Sample Extraction

Aqueous samples can be extracted by LLE or by SPE. The latter offers certain advantages over the LLE. The SPE reduces the solvent consumption and eliminates the problem of emulsion. The procedure for this extraction is described below.

The cartridge is loaded first with 5 mL acetone. Vacuum is applied and the eluant is discarded. Repeat these steps first with 5 mL 0.1 M and then with 5 mL of 0.02 M potassium hydrogen phosphate (K_2HPO_4), respectively. The sorbent should not be allowed to go dry. Add the sample to the cartridge from a sample reservoir attached to the top of the cartridge. Remove the reservoir and rinse the cartridge with 3 mL of 40:60 methanol–water mixture while applying vacuum. Discard the eluant. Centrifuging the cartridge may be performed to remove additional water to concentrate the sample. Analytes are now eluted from the cartridge with 3 mL acetone. Use vacuum for this. Collect the eluant and concentrate the solution to dryness under a stream of nitrogen and mild heat. The residue is dissolved in 200 μL of acetone for GC analysis or 200 μL of acetonitrile for HPLC analysis.

46 Pesticides
Organochlorine

Organochlorine pesticides refer to all chlorine-containing organics used for pest control. The term, however, is not confined to compounds of any single and specific type of chemical structures or organic functional group(s), but includes a broad range of substances. The grouping together of these compounds is more or less based on the similarity in their chemical analysis. Many chlorinated pesticides that were commonly used in the past are no longer being used now, because of their harmful toxic effect on humans and the contamination of the environment. Many such pesticides and their residues are still found in the environment in trace quantities in groundwater, soil, sediments, and wastewater. These substances are stable, bioaccumulative, and toxic, and some are also carcinogens (Patnaik, 2007). Table 46.1 presents some common chlorinated pesticides, most of which are listed as priority pollutants by U.S. EPA.

Chlorinated pesticides in aqueous and nonaqueous matrices may be determined by U.S. EPA Methods 608, 625, 505, 508, 8080, and 8270 (U.S. EPA 1984–1994). Analysis of these pesticides requires the extraction of the aqueous or nonaqueous samples by a suitable organic solvent, concentration, and cleanup of the extracts, and the determination of the analytes in the extracts, usually by GC-ECD or GC/MS. These steps are outlined below.

SAMPLE EXTRACTION

Aqueous samples are extracted with hexane or with methylene chloride by LLE using a separatory funnel or a mechanical shaker, or by microextraction. Aqueous samples can also be extracted by SPE using a C-18 cartridge. The selection of sample volume should be based on the extent of sample concentration that may be needed to achieve the required detection level in the analysis, as well as the use of a packed or capillary column. A larger sample concentration is required for packed column than that for capillary column analysis. The U.S. EPA recommends the extraction of 1 L sample to a final volume of 1 mL for wastewater analysis performed on a packed column. For the analysis of potable water by GC-ECD on a capillary column, the concentration of a 35 mL sample aliquot to a final volume of 2 mL by microextraction is sufficient to produce the required detection range for the pesticides. If the sample extracts were to be analyzed by GC/MS, the extraction solvent can be methylene chloride or hexane. On the other hand, if a GC-ECD is used, a nonchlorinated solvent such as hexane or isooctane should be used for extraction. Alternatively, a chlorinated solvent, such as methylene chloride can be used, but the extract must be exchanged into hexane or isooctane if analyzed by GC-ECD. In SPE, the aqueous sample is passed through the cartridge after cleaning the cartridge with acetone and methanol. Pesticides adsorbed on the sorbent are eluted with acetone. The eluant is concentrated to dryness. The residue is dissolved in acetone or any other suitable solvent for GC analysis.

Sonication or Soxhlet extraction using the solvents mentioned above extracts soil, sediment, and solid waste samples. The sample should be mixed with anhydrous Na_2SO_4 before extraction.

The solvent extract should be subjected to one or more cleanup steps for the removal of interfering substances. The presence of phthalate esters, sulfur, or other chlorinated compounds can mask pesticide peaks. Therefore, the extract should be cleaned up of the interfering substances using a Florisil column or by gel permeation chromatography (see Chapter 5). The distribution patterns for the pesticides in the Florisil column fractions are presented in Table 46.2.

TABLE 46.1
Some Common Chlorinated Pesticides and Their Degradation Products

CAS No.	Common Name
[15972-60-8]	Alachlor
[309-00-2]	Aldrin
[1912-24-9]	Atrazine
[319-84-6]	α-BHC
[319-85-7]	β-BHC
[319-86-8]	δ-BHC
[58-89-9]	γ by BHC (Lindane)
[133-06-2]	Captan
[57-74-9]	Chlordane
[5103-71-9]	α-Chlordane
[5103-74-2]	γ-Chlordane
[2675-77-6]	Chlorneb
[510-15-6]	Chlorobenzilate
[1897-45-6]	Chlorothalonil
[1861-32-1]	DCPA (Dacthal)
[72-54-8]	4,4′-DDD
[72-55-9]	4,4′-DDE
[50-29-3]	4,4′-DDT
[60-57-1]	Dieldrin
[99-30-9]	Dichloran
[72-20-8]	Endrin
[7421-93-4]	Endrin aldehyde
[53494-70-5]	Endrin ketone
[959-98-8]	Endosulfan-I
[33213-65-9]	Endosulfan-II
[1031-07-8]	Endosulfan sulfate
[2593-15-9]	Etridiazole
[76-44-8]	Heptachlor
[1024-57-3]	Heptachlor epoxide
[118-74-1]	Hexachlorobenzene
[77-47-4]	Hexachlorocyclopentadiene
[72-43-5]	Methoxychlor
[2385-85-5]	Mirex
[39765-80-5]	*trans*-Nonachlor
[54774-45-7]	*cis*-Permethrin
[51877-74-8]	*trans*-Permethrin
[1918-16-7]	Propachlor
[122-34-9]	Simazine
[8001-35-2]	Toxaphene
[1582-09-8]	Trifluralin

An additional cleanup step should be performed to remove sulfur using mercury or copper powder. Permanganate–sulfuric acid treatment is not recommended. Unlike PCBs, most pesticides are fully or partially oxidized by reaction with $KMnO_4$–H_2SO_4. Treatment with concentrated H_2SO_4 alone is not recommended, because pesticides such as dieldrin and endrin were found to be totally

TABLE 46.2
Elution Patterns for Pesticides in Florisil Column Cleanup

	Percent Recovery by Fraction		
Pesticides	**6% Ether in Hexane**	**15% Ether in Hexane**	**50% Ether in Hexane**
β-BHC	97	–	–
Δ-BHC	98	–	–
γ-BHC (Lindane)	100	–	–
Chlordane	100	–	–
4,4′-DDD	99	–	–
4,4′-DDE	98	–	–
4,4′DDT	100	–	–
Dieldrin	–	100	–
Endosulfan I	37	64	–
Endosulfan II	–	7	91
Endosulfan sulfate	–	–	100
Endrin	4	96	–
Endrin aldehyde	–	68	26
Heptachlor epoxide	100	–	–
Toxaphene	96	–	–

destroyed at 20 ng/mL and endrin aldehyde and endosulfan sulfate partially decomposed at 60 ng/mL concentrations, respectively, in the extract.

Accuracy of the extraction and analytical method may be evaluated from the surrogate spike recovery. Compounds recommended as surrogates are dibutyl-chlorendate, tetrachloro-*m*-xylene, 4,4′-dichlorobiphenyl, 2-fluorobiphenyl, 2,4,6-tribromophenol, hexabromobenzene, and *o*,*p*-DDE. The latter is found to be suitable in the packed column analysis without any coelution problem and with a retention time close to the pesticides in the midrange of the chromatogram of the pesticide mixture (Cavanaugh and Patnaik, 1995). Any other stable chlorinated organics that do not decompose or oxidize under the conditions of extraction and analysis and that exhibit good response to halogen-specific detectors may also be used as surrogates. The surrogate spike recovery should fall within 70%–130%.

ANALYSIS

Organochlorine pesticides in the solvent extract are analyzed either by GC using a halogen-specific detector, most commonly ECD or by GC/MS. It may be also analyzed by GC-FID. All the U.S. EPA methods are based on GC-ECD and GC/MS determination. Compounds identified by GC on a specific column must be confirmed on an alternate column. Alternately, the presence of pesticides can be confirmed by analyzing on GC/MS. After qualitatively identifying and confirming the pesticide peaks, quantitation should be performed by GC-ECD using either the internal standard or the external standard method. When the internal standard method is followed, use more than one internal standard, all of which should have chromatographic responses comparable to the analytes of interest and have retention times covering the entire range of chromatogram. Pentachloronitrobenzene, 4,4′-dichlorobiphenyl, and 4,4′-dioromooctafluorobiphenyl are some examples of internal standards.

A single point calibration may be used instead of a working calibration curve for quantitation by either the external or the internal standard method if the response from the single point standards

produces a response that deviates from the sample extract response by no more than 20%. The solvent for preparing calibration standards should preferably be the same one used to make the final sample extract. Hexane, isooctane, or methyl-*tert*-butyl ether is an appropriate solvent for the analysis of chlorinated pesticides by GC-ECD.

Chlorinated pesticides mixture can be separated on both packed and capillary columns. Some of the columns and conditions are as follows:

- Packed column: 1.8 m long × 4 mm ID glass column packed with (1) 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or (2) 3% OV-1 on Supelcoport (100/120 mesh) or equivalent.
- Carrier gas: 5% methane/95% argon at 60 mL/min; temperature: oven 200°C (isothermal), injector 250°C, and ECD 320°C.
- Capillary column: silicone-coated fused silica 30 m (or other length) × 0.53 mm (or 0.32 or 0.25 mm) ID × 1.5 μm (or 0.83 μm) film thickness, such as DB-608, SPB-608, DB-5, Rtx-5, DB-17, or equivalent.
- Carrier gas: He 35 cm/s, makeup gas N_2 30 mL/min; temperature: 140°C–260°C at 5°C–10°C/min, injector 250°C, and ECD 325°C. Other temperature and flow rate conditions suitable for the analysis may be used.

The presence of a pesticide determined on one column must be confirmed on an alternate column. In addition, certain pesticides coeluting on one column can be separated by using another column. For example, 4,4′-DDD and endosulfan-II coeluting on SP-2250/SP-2401 can be effectively separated on the OV-1 packed column. Conversely, 4,4-DDE and dieldrin coeluting on OV-1 are better separated on SP-2250/SP-2401 column. Many chlorinated pesticides may coelute even on a 30 m long, 0.53 mm ID, and 1.5 μm film capillary column. This includes the following pairs on a DB-5 column (J&W Scientific, 2009):

1. Aldrin and DCPA
2. γ-Chlordane and *o*,*p*-DDE
3. α-Chlordane and endosulfan-I
4. Chlorobenzillate and endrin
5. *p*,*p*′-DDT and endosulfan sulfate

These coeluting pairs, however, can be separated distinctly on the same column with a smaller film thickness, 0.83 μm.

Two common pesticides endrin and DDT are susceptible to decomposition on a dirty injection port. The former oxidizes to endrin aldehyde and endrin ketone, while the latter degrades to 4,4′-DDE and 4,4′-DDD. If degradation of either of these analytes exceeds 20%, corrective action should be taken before performing calibration. The percent breakdown is calculated as follows:

$$\%\ \text{Breakdown for endrin} = 100 \times \frac{\text{Peak areas of endrin aldehyde} + \text{Endrin ketone}}{\text{Peak areas of endrin} + \text{Endrin aldehyde} + \text{Endrin ketone}}$$

$$\%\ \text{Breakdown for DDT} = 100 \times \frac{\text{Peak areas of DDE} + \text{DDD}}{\text{Peak areas of DDT} + \text{DDE} + \text{DDD}}$$

A standard containing the pure compounds endrin and DDT should be injected to determine the possible breakdown.

The pesticides in the solvent extract may also be analyzed by GC-FID. On a DB-5 capillary column (30 m × 0.25 mm ID × 0.25 μm), for example, a pesticide mixture at 2 μL split less injection

may be analyzed at a hydrogen (carrier gas) flow of 43 cm/s, N_2 makeup gas flow of 30 mL/min and at an oven temperature programmed from 50°C to 300°C. Other columns or conditions may be used. The instrument detection limit for FID is, however, higher than that for the ECD.

The confirmation of pesticides by GC/MS should be more reliable than that on the GC-ECD using an alternate column. The presence of stray interference peaks, even after sample cleanup, and the retention time shift and coelution problem, often necessitates the use of GC/MS in the identification of compounds. If a quantitative estimation is to be performed, select the primary ion or one of the major characteristic ions of the compounds and compare the area response of this ion to that in the calibration standard. Quantitation, however, is generally done from the GC-ECD analysis, because ECD exhibits a much greater sensitivity than the MSD. For example, while ECD

TABLE 46.3
Characteristic Masses for Chlorinated Pesticides

Pesticides	Primary Ion *m/z*	Secondary Ions *m/z*
Aldrin	66	263, 220
Atrazine	200	215
α-BHC	183	181, 109
β-BHC	181	183, 109
δ-BHC	183	181, 109
γ-BHC (Lindane)	183	181, 109
Captan	79	149, 77, 119
α-Chlordane	375	377
γ-Chlordane	375	377
Chlorobenzilate	251	139, 253, 111, 141
4,4′-DDD	235	237, 165
4,4′-DDE	246	248, 176
4,4′-DDT	235	237, 165
Dieldrin	79	263, 279
Endosulfan I	195	339, 341
Endosulfan II	337	339, 341
Endosulfan sulfate	272	387, 422
Endrin	263	82, 81
Endrin aldehyde	67	345, 250
Endrin ketone	317	67, 319
Heptachlor	100	272, 274
Heptachlor epoxide	253	355, 351, 81
Hexachlorobenzene	284	142, 249
Hexachlorocyclopentadiene	237	235, 272
Methoxychlor	227	228, 152, 114, 274
Mirex	272	237, 274, 270, 239
trans-Nonachlor	409	
Simazine	201	
Toxaphene	159	231, 233
Trifluralin	306	43, 264, 41, 290
	Surrogates	
2-Fluorobiphenyl	172	171
2-Fluorophenol	112	64
Terphenyl-d_{14}	244	122, 212
2,4,6-Tribromophenol	330	332, 141

is sensitive to 0.01 ng dieldrin, the lowest MSD detection for the same compound is in the range of 1 ng. The primary and secondary characteristic ions for qualitative identification and quantitation are presented in Table 46.3. The data presented are obtained under MS conditions utilizing 70 V (nominal) electron energy under the electron-impact ionization mode.

AIR ANALYSIS

The NIOSH and the U.S. EPA methods (U.S. EPA 1984–1988, NIOSH, 1984–1989) may analyze most of the organochlorine pesticides listed in this chapter. The method of analysis, in general, involves drawing a measured volume of air through a sorbent cartridge containing polyurethane foam or Chromosorb 102. The pesticides are extracted with an organic solvent such as toluene, hexane, or diethyl ether; the extract concentrated and analyzed by GC-ECD. The extract may be cleaned up by Florisil to remove any interference (U.S. EPA Method 608).

A very low detection limit, >1 ng/m^3 may be achieved using a 24 h sampling period, sampling over 5000 L ambient air. Such a high volume sampler consists of a glass fiber filter with a polyurethane foam backup absorbent cartridge (U.S. EPA Method TO4). A low volume (1–5 L/min) sampler consisting of a sorbent cartridge containing polyurethane foam may be used to collect pesticide vapors (U.S. EPA Method TO10). Pesticides are extracted with an ether–hexane mixture and analyzed by GC-ECD. Pesticides in the extract may be determined by GC using other detectors as well, such as HECD or by a mass spectrometer. Certain pesticides may be analyzed by GC-FPD, GC-NPD, or by HPLC using an UV or an electrochemical detector.

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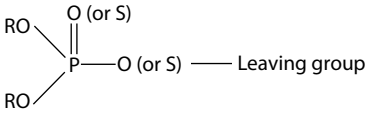
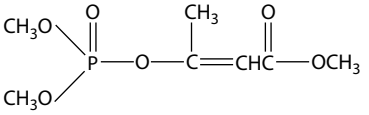
47 Pesticides
Organophosphorus

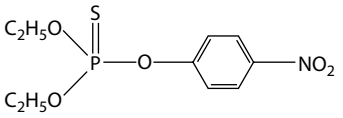
An important class of pesticides is organophosphorus compounds, which have the following general structure:



where *R* is an alkyl or aryl group. The phosphorus atom in such a compound is bound to one or two oxygen and/or sulfur atom(s). The leaving group may be any organic species that may cleave out from its oxygen or sulfur bond. Two typical examples are as follows:



(Mevinphos)



(Parathion)

Organic phosphates can cause moderate-to-severe acute poisoning. These substances inhibit the function of the enzyme, acetylcholinesterase by phosphorylating or binding the enzyme at its esteratic site. The symptoms of acute toxicity include tightening of the chest, increased salivation and lacrimation, nausea, abdominal cramps, diarrhea, pallor, the elevation of blood pressure, headache, insomnia, and tremor. The ingestion of large quantities may cause convulsions, coma, and death. The toxicity, however, varies from substance to substance. Phorate, demeton, and disulfoton are among the most toxic organophosphorus insecticides, while malathion, ronnel, and tokuthion are much less toxic.

ANALYSIS OF AQUEOUS AND SOLID SAMPLES

GC and GC/MS techniques are the most common instrumental methods to analyze organophosphorus pesticides. These substances may also be analyzed by HPLC. However, there are no systematic precision and accuracy studies published on the HPLC determination of environmental samples. The detector required for GC analysis is either a NPD operated in the phosphorus specific mode, or a FPD operated in the phosphorus-specific mode.* Thus, any pesticide can be analyzed by GC-NPD or GC-FPD using a suitable capillary column as listed below. Some of the common pesticides are listed in Table 47.1. A halogen-specific detector, such as electrolytic conductivity or microcoulometric detector, may alternatively be used for GC analysis of only those pesticides that contain halogen atoms. Some of these halogen-containing organophosphorus pesticides are presented in Table 47.2.

* FPD measures the phosphorus or sulfur-containing substances. Because most organophosphorus pesticides contain sulfur atoms, the FPD may be more sensitive and selective. Both these detectors may be used in a dual column dual detector system for analysis.

TABLE 47.1
Common Organophosphorus Pesticides

CAS No.	Pesticides	Alternate Name(s)
[30560-19-1]	Acephate	Orthene
[21548-32-3]	Acconame	Geofos, Fosthietan
[1757-18-2]	Akton	–
[3244-90-4]	Aspon	–
[86-50-0]	Azinphos methyl	Guthion
[2642-71-9]	Azinphos ethyl	Guthion ethyl
[35400-43-2]	Bolstar	Sulprophos
[122-10-1]	Bomyl	Swat
[786-19-6]	Carbofenothion	Trithion
[470-90-6]	Chlorfenvinphos	Birlane
[56-72-4]	Coumaphos	Muscatox
[7700-17-6]	Crotoxyphos	Ciodrin
[8065-48-3]	Demeton-O,S	Systox
[333-41-5]	Diazinon	Neocidol
[2463-84-5]	Dicapthon	–
[97-17-6]	Dichlofenthion	Nemacide VC-13
[62-73-7]	Dichlorvos	Nerkol
[141-66-2]	Dicrotophos	Carbicron
[60-51-5]	Dimethoate	Cygon
[78-34-2]	Dioxathion	Navadel
[298-04-4]	Disulfoton	Thiodemeton
[2921-88-2]	Dursban	Trichlorpyrphos, Chlorpyrifos
[2104-64-5]	EPN	–
[563-12-2]	Ethion	Nialate
[16672-87-0]	Ethephon	Ethrel
[52-85-7]	Famphur	Famophos
[22224-92-6]	Fenamiphos	–
[122-14-5]	Fenitrothion	Folithion
[115-90-2]	Fensulfothion	Terracur P
[55-38-9]	Fenthion	Entex
[944-22-9]	Fonofos	Dyfonate
[42509-80-8]	Isazophos	Miral
[25311-71-1]	Isofenphos	Oftanol
[21609-90-5]	Leptophos	Lepton, Phosvel
[121-75-5]	Malathion	Cythion
[150-50-5]	Merphos	–
[10265-92-6]	Methamidophos	Tamaron
[950-37-8]	Methidathion	Supracide
[7786-34-7]	Mevinphos	Phosdrin
[6923-22-4]	Monocrotophos	Azodrin
[299-86-5]	Montrel	Crufomate, Ruelene
[300-76-5]	Naled	Dibrom
[301-12-2]	Oxydemeton-methyl	Meta Systox-R
[56-38-2]	Parathion-ethyl	Paraphos
[298-00-0]	Parathion-methyl	Nitran
[311-45-5]	Paraoxon	Phosphacol

(*Continued*)

TABLE 47.1 (*Continued*)
Common Organophosphorus Pesticides

CAS No.	Pesticides	Alternate Name(s)
[22224-92-6]	Phenamiphos	Nemacur
[298-02-2]	Phorate	Thimet
[2310-17-0]	Phosalone	Rubitox, Azofene
[947-02-4]	Phosfolan	Cylan
[13171-21-6]	Phosphamidon	Dimecron
[732-11-6]	Phosmet	Prolate, Imidan
[41198-08-7]	Profenofos	Curacron
[31218-83-4]	Propetamphos	Safrotin
[13194-48-4]	Prophos	Phosethoprop
[299-84-3]	Ronnel	Fenchlorphos, Etrolene
[3689-24-5]	Sulfotepp	–
[107-49-3]	TEPP	Tetron, Tetraethyl pyrophosphate
[13071-79-9]	Terbufos	Counter
[22248-79-9]	Tetrachlorvinphos	Stirophos
[3383-96-8]	Tetrafenphos	Abate, Temephos
[297-97-2]	Thionazin	Zinophos, Namafos
[34643-46-4]	Tokuthion	Protothiophos
[52-68-6]	Trichlorfon	Anthon, Chlorofos
[327-98-0]	Trichloronate	–

TABLE 47.2
Organophosphorus Pesticides Containing Halogen Atoms

CAS No.	Pesticides	Halogen Atoms in the Molecule
[1757-18-2]	Akton	3
[786-19-6]	Carbofenothion (Trithion)	1
[470-90-6]	Chlorfenvinphos	3
[56-72-4]	Coumaphos	1
[2463-84-5]	Dicapthen	1
[97-17-6]	Dichlofenthion	2
[62-73-7]	Dichlorvos	2
[2921-88-2]	Dursban (Chlorpyrifos)	3
[16672-87-0]	Ethephon (Ethrel)	1
[21609-90-5]	Leptophos	3
[5598-13-0]	Methyl dursban (Methyl chlorpyrifos)	3
[115-78-6]	Phosphan	3
[41198-08-7]	Profenofos	2
[299-84-3]	Ronnel (Fenchlorphos)	3
[22248-79-9]	Tetrachlorvinphos (Stirofos)	4
[52-68-6]	Trichlorfon (Anthon)	3

TABLE 47.3
Characteristic Ions for Identification of Some Common Organophosphorus Pesticides by GC/MS[a]

CAS No.	Pesticides	Primary Ion (*m/z*)	Secondary Ions (*m/z*)
[86-50-0]	Azinphos-methyl	160	132,93,104,105
[35400-43-2]	Bolstar	156	140,143,113,33
[786-19-6]	Carbofenothion	157	97,121,342,159,199
[470-90-6]	Chlorfenvinphos	267	269,323,325,295
[56-72-4]	Coumaphos	362	226,210,364,97,109
[7700-17-6]	Crotoxyphos	127	105,193,166
[298-03-3]	Demeton-O	88	89,60,61,115,171
[126-75-0]	Demeton-S	88	60,81,114,115,89
[333-41-5]	Diazinon	137	179,152,93,199,304
[62-73-7]	Dichlorovos	109	185,79,145
[141-66-2]	Dicrotophos	127	67,72,109,193,237
[60-51-5]	Dimethoate	87	93,125,143,229
[298-04-4]	Disulfoton	88	97,89,142,186
[2921-88-2]	Dursban	197	97,199,125,314
[2104-64-5]	EPN	157	169,185,141,323
[563-12-2]	Ethion	231	97,153,125,121
[52-85-7]	Famphur	218	125,93,109,217
[115-90-2]	Fensulfothion	293	97,308,125,292
[55-38-9]	Fenthion	278	125,109,169,153
[21609-90-5]	Lephtophos	171	377,375,77,155
[121-75-5]	Malathion	173	125,127,93,158
[298-00-0]	Methyl parathion	109	125,263,79,93
[150-50-5]	Merphos	209	57,153,41,298
[7786-34-7]	Mevinphos	127	192,109,67,164
[6923-22-4]	Monocrotophos	127	192,67,97,109
[300-76-5]	Naled	109	145,147,301,79
[56-38-2]	Parathion	109	97,291,139,155
[298-02-2]	Phorate	75	121,97,93,260
[2310-17-0]	Phosalone	182	184,367,121,379
[732-11-6]	Phosmet	160	77,93,317,76
[13194-48-4]	Prophos	158	43,97,41,126
[13171-21-6]	Phosphamidon	127	264,72,109,138
[3689-24-5]	Sulfotepp	322	97,65,93,121,202
[13071-79-9]	Terbufos	231	57,97,153,103
[22248-79-9]	Tetrachlorvinphos	109	329,331,79,333
[107-49-3]	Tetraethyl pyrophosphate	99	155,127,81,109
[297-97-2]	Thionazin	107	96,97,163,79,68
[34643-46-4]	Tokuthion	113	43,162,267,309
[512-56-1]	Trimethyl phosphate	110	79,95,109,140
[78-32-0]	Tri-*p*-tolyl phosphate	368	367,107,165,198
[126-72-7]	Tris (2,3-dibromopropyl) phosphate	201	137,119,217,219,199

Note: A fused silica capillary column is recommended. Column type and conditions are presented earlier in this chapter.

[a] GC/MS conditions: electron impact ionization; nominal energy 70 eV; mass range 35–500 amu; scan time 1 s/scan.

The analysis of organophosphorus pesticides by GC/MS should be the method of choice wherever possible. This is a confirmatory test to identify the compounds from their characteristic ions in addition to their retention times. Table 47.3 lists the primary and secondary characteristic ions of some common organophosphorus pesticides.

1. The pesticides listed above can be analyzed by GC-FPD (in P-mode) or by GC/MS following extractions. An open, tubular fused silica capillary column (35 m and 0.53 ID) gives better resolution and sensitivity than a packed column. Some compounds may coelute, which should be analyzed on an alternative column.
2. Precision and accuracy must be established for the analytes before their analysis.
3. Extraction should be performed immediately for substances such as TEPP, terbufos, and diazinon, which are unstable in water.
4. The recovery is poor for naled and trichlorfon, both of which may be converted to dichlorvos during extraction or on the GC column. The latter compound also shows poor recovery because its solubility is relatively high in water.
5. Demeton-O,S is a mixture of two isomers, giving two peaks. Merphos often gives two peaks due to its oxidation.
6. Many of the above substances are not in the U.S. EPA's list of priority pollutants. No EPA methods are available for these unlisted compounds.

Sample Extraction

Aqueous samples are extracted with methylene chloride using a separatory funnel or a continuous liquid–liquid extractor. Solid samples are extracted with methylene chloride–acetone mixture (1:1) by either sonication or Soxhlet extraction. The methylene chloride extract should be finally exchanged to hexane or isooctane or MTBE. The latter solvents should be mixed with acetone during solvent exchange. The extracts should then be cleaned up by using Florisil. Often the Florisil cleanup reduces the percent recovery of the analyte to less than 85%. A preliminary screening of the extract should therefore be done to determine the presence of interference and the necessity of Florisil cleanup. Gel permeation cleanup also lowers the analyte recovery and thus is not recommended. If a FPD is used in the GC analysis, the presence of elemental sulfur can mask the analyte peaks. In such a case, sulfur cleanup should be performed. Sample extraction and cleanup procedures are described in Chapter 5.

The extract should be then injected onto the GC column for GC or GC/MS analysis. If internal standard calibration is performed, spike three or more internal standards into the sample extract. Any organophosphorus pesticides whose analysis is not required or which are not found to be present in the screening test may be used as an internal standard. The chromatographic columns and conditions are presented below:

- Column: DB-5, DB-210, SPB-5, SPB-608, or equivalent (wide-bore capillary columns)
- Carrier gas: Helium, 5 mL/min
- Temperature: 50°C for 1 min; 5°C/min to 140°C, held for 10 min; 10°C/min to 240°C, and held for 15 min.

If any pesticide is detected, its presence must be confirmed on a second GC column or by GC/MS. The detection limits, as well as the precision and accuracy of all analytes of interest must be determined before the analysis. Organophosphorus pesticides other than those listed under U.S. EPA's priority pollutants can also be analyzed by the above procedure if the precision and accuracy data of these substances are within the reasonable range of acceptance. Such acceptance criteria have not yet been published for a number of substances of this class. The spike recovery may vary from substance

to substance, and is matrix dependent. However, in all cases, the precision, accuracy, and the detection limits of analytes should be established before the analysis.

AIR ANALYSIS

Air analysis for some of the individual pesticides of this class has been published by NIOSH. These pesticides include mevinphos, TEPP, ronnel, malathion, parathion, EPN, and demeton (NIOSH Methods 2503, 2504, 1450). In general, pesticides in air may be trapped over various filters, such as Chromosorb 102, cellulose ester, XAD-2, PTFE membrane (1 μm), or a glass fiber filter. The analyte(s) are extracted from the filter or the sorbent tube with toluene or any other suitable organic solvent. The extract is analyzed by GC (using a NPD or FPD) or by GC/MS. The column conditions and the characteristic ions for compound identifications are presented in the preceding section. Desorption efficiency of the solvent should be determined before the analysis by spiking a known amount of the analyte into the sorbent tube or filter and then measuring the spike recovery.

REFERENCE

NIOSH Methods 2503, 2504, and 1450. *NIOSH Manual of Analytical Methods*, 4th edition and supplements updates. Cincinnati, OH: National Institute for Occupational Safety and Health.

48 pH and Eh

pH is a measure of hydrogen ion [H^+] concentration in an aqueous solution. It is defined as

$$pH = \log \frac{1}{[H^+]} = -\log[H^+]$$

Similarly, hydroxide ion [OH^-] concentration may be expressed as pOH, which is

$$\log \frac{1}{[OH^-]} \quad \text{or} \quad -\log[OH^-]$$

The concentrations [H^+] and [OH^-] are expressed in molarity (M or mol/L). In a neutral solution, pH = pOH = 7. The sum of pH and pOH is 14.0.

In an acidic solution, the hydrogen ion concentration is greater than 1.0×10^{-7} M, and thus the pH is less than 7. Similarly, in a basic solution, the [H^+] is less than 1.0×10^{-7} M and, therefore, the pH is greater than 7.

The pH of a solution of a strong acid or a strong base can be calculated. Conversely, [H^+] and [OH^-] can be determined from the measured pH of the solution. This is shown in the following examples.

EXAMPLE 48.1

What is the pH of a solution of 0.005 M HCl?

Because HCl is a strong acid, it will completely dissociate into H^+ and Cl^- ions. Thus, 0.005 M HCl will dissociate into 0.005 M H^+ and 0.005 M Cl^- ions.

$$pH = -\log[H^+]$$

Substituting the value for [H^+]

$$pH = -\log[0.005] = 2.30$$

EXAMPLE 48.2

0.655 g KOH was dissolved in reagent grade water and made up to a volume of 500 mL. What is the pH of this KOH solution prepared?

First, we calculate the molarity of this solution as follows:

$$\frac{0.655\ \text{g KOH}}{500\ \text{mL soln}} \times \frac{1\ \text{mol KOH}}{39\ \text{g KOH}} \times \frac{1000\ \text{mL soln}}{1\text{L soln}} = 0.0336\ \text{mol KOH/L soln. or } 0.0336\ \text{M KOH}$$

Because KOH is a strong base, it will completely dissociate into K^+ and OH^- ions. Thus, 0.0336 M KOH will dissociate, producing 0.0336 M K^+ and 0.0336 M OH^- ions.

$$\text{Thus, pOH} = -\log[OH^-] \quad \text{or} \quad -\log[0.0336]$$
$$= 1.47$$

$$\text{Therefore, pH} = 14.00 - 1.47$$
$$= 12.53$$

This problem may also be solved as follows:
We know that $K_w = [H^+][OH^-]$. K_w is always 1.0×10^{-14} M; $[OH^-] = 0.0336$ M; $[H^+] = ?$

$$[H^+] = \frac{1.0\times10^{-14}}{0.0336} \quad \text{or} \quad \frac{1.0\times10^{-14}}{3.36\times10^{-2}}$$
$$= 2.98\times10^{-13}\text{M}$$

$$\text{pH} = -\log(2.98\times10^{-13})$$
$$= -(0.47 - 13)$$
$$= 12.53$$

The pH of an aqueous sample may be measured by the electrometric or colorimetric method. The latter, which involves the use of pH indicator papers, could measure the pH between 2 and 12 within a fairly accurate degree of approximation. A pH below 10 may be determined to two significant figures and that of 10 and above may be measured to three significant figures. However, for environmental analysis, which requires a very high degree of accuracy and precision, pH is determined by the electrometric method. This electrometric technique determines the activity of the hydrogen ions by potentiometric measurement by means of a glass sensor electrode (of a hydrogen electrode) and a reference electrode (calomel or silver: silver chloride electrode). The electromotive force (emf) produced varies linearly with the pH.

The pH meter used for pH measurement consists of these glass and reference electrodes and a potentiometer for measuring the electrode potential. The pH meter must be daily calibrated against the standard buffer solutions of pH 4, 7, and 10. pH measurements are affected by temperature and the presence of very high concentrations of suspended matter.

Soil pH is determined by mixing the soil with reagent grade water (1:1), stirring the solution, allowing the soil to settle down, and then recording the pH of the supernatant liquid. Experimental evidences, however, indicate a significant variation in pH values by changing the soil to water ratio. An accurate method of pH determination in soil involves the ion exchange of H^+ ions present in the soil with Ca^{2+} ions added into the soil sample. A saturated solution of $CaCl_2$ in neutral water is added to an aliquot of soil. The mixture is stirred and allowed to stand. Ion exchange occurs between Ca^{2+} ions in the solution and H^+ ions in the soil. Hydrogen ions are released from the soil into the solution. The pH of the supernatant $CaCl_2$ solution containing the released H^+ ion is measured.

Eh

Eh is a measure of oxidation–reduction potential in the solution. The chemical reactions in the aqueous system depend on both the pH and the Eh. While pH measures the activity (or concentration) of hydrogen ions in the solution, Eh is a measure of the activity of all dissolved species. Aqueous solutions contain both oxidized and reduced species. For example, if iron is present in the solution, there is a thermodynamic equilibrium between its oxidized and reduced forms. Thus, at the redox equilibrium, the reaction is as follows:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

The electron activity (or intensity) at the redox equilibrium may be measured by a potentiometer. A pH meter or a millivoltmeter may be used for measuring the potential difference between a reference electrode (such as a calomel electrode) and an oxidation–reduction indicator electrode (such as platinum, gold, or a wax-impregnated graphite electrode).

Samples must be analyzed immediately, preferably at the sampling site. Avoid exposure to air because it can oxidize any reduced species present in the sample.

The platinum electrode is most commonly used with the Ag:AgCl reference electrode with KCl as the electrolyte. The electrode system should be first standardized against a standard redox solution before the Eh of the sample is measured. The procedure for Eh determination is outlined below:

1. Prepare one of the following redox standard solutions as follows:
   Standard A: dissolve 1.4080 g potassium ferrocyanide [$K_3Fe(CN)_6 \cdot 3H_2O$], 1.0975 g potassium ferricyanide [$K_3Fe(CN)_6$], and 7.4555 g KCl in reagent grade water and dilute the solution to 1 L.
   Standard B: dissolve 39.21 g ferrous ammonium sulfate [$Fe(NH_4)_2\ (SO_4)_2 \cdot 6H_2O$] and 48.22 g ferric ammonium sulfate [$Fe(NH_4)\ (SO_4)_2 \cdot 12H_2O$] in reagent grade water; slowly add 56.2 mL conc. H_2SO_4; dilute the solution to 1 L.
   Redox standard solutions are also commercially available.
2. Measure the potential of this redox standard solution following the manufacturer's instructions for using the pH meter or the millivoltmeter.
3. Measure the potential of the sample in the same way.
4. Record the temperature of the sample.

Eh can be determined from the following equation:

$$\text{Eh} = E_1 + E_2 - E_3$$

where

E_1 is the sample potential relative to the reference electrode

E_2 is the theoretical Eh of the reference electrode and the redox standard solution relative to the standard hydrogen electrode (E_2 may be calculated, see below)

E_3 is the observed potential of the redox standard solution, relative to the reference electrode

TABLE 48.1
Potentials of Redox Standard Solutions for Selected Reference Electrodes

	Potential in Millivolts for Redox Standard Solutions at 25°C	
Electrode System (Indicator-Reference)	**Standard A**	**Standard B**
Platinum–calomel (Hg: $HgCl_2$ saturated KCl)	+183	+430
Platinum–Ag:AgCl (1 M KCl)	+192	+439
Platinum–Ag:AgCl (saturated KCl)	+229	+476
Platinum–hydrogen	+428	+675

E_2, the theoretical Eh of the reference electrode, may be calculated from the stability constants. For each 1°C increase in temperature, the potential of $K_4Fe(CN)_6$–$K_3Fe(CN)_6$–KCl solution shows a decrease of about 2 mV. The Eh of this redox standard solution for the platinum electrode versus Ag:AgCl reference electrode may be calculated as follows:

$$\text{Eh}\,(\text{mV}) = 428 - 2.2(T - 25)$$

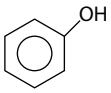
where T is the temperature of the solution.

The potentials of the platinum electrode versus various reference electrodes for redox standard solutions A and B are presented in Table 48.1.

The oxidation–reduction potential is sensitive to pH. The Eh decreases with an increase in the pH and increases with a decrease in the pH, if H^+ ion or OH^- ion is involved in the redox half-cells.

49 Phenols

Phenols are organic compounds containing an −OH group attached to an aromatic ring. The structure of phenol, the prototype compound of this class, is



Although the presence of other substituents in the ring can produce an array of diverse compounds of entirely different properties, the chemical analysis of most phenols, however, can be performed in the same way. This is attributed to (1) the acidic nature of the phenolic −OH group and (2) the ability of −OH groups to form derivatives.

Trace amounts of phenols may occur in many natural waters as well as in domestic and industrial wastewater. The chlorination of such waters can produce chlorophenols.

Several phenolic compounds occurring in industrial wastewater, soil, sediments, and hazardous waste are classified as U.S. EPA priority pollutants. These are presented in Table 49.1.

The total phenolic compounds in an aqueous sample can be determined by a colorimetric method using 4-aminoantipyrine. This reagent reacts with phenolic compounds at pH 8 in the presence of potassium ferricyanide to form a colored antipyrine dye, the absorbance of which is measured at 500 nm. The antipyrine dye may also be extracted from the aqueous solution by chloroform. The absorbance of the chloroform extract is measured at 460 nm. The sample may be distilled before analysis for the removal of interfering nonvolatile compounds. The above colorimetric method determines only *ortho*- and *meta*-substituted phenols and not all phenols. When the pH is properly adjusted, certain *para*-substituted phenols that include methoxyl-, halogen-, carboxyl-, and sulfonic acid substituents, may be analyzed too.

The individual phenolic compounds may be determined by GC-FID or GC/MS. Alternately, the phenol may be derivatized to a halogen derivative and measured by GC-ECD.

EXTRACTION

Aqueous samples are extracted with methylene chloride. If the sample is not clean or if the presence of organic interference is suspected, a solvent wash should be performed. For this, the pH of the sample is adjusted to 12 or greater with NaOH solution. The sample solution made basic is then shaken with methylene chloride. The organic contaminants of a basic nature and most neutral substances, partition into the methylene chloride phase, leaving the phenols and other acidic compounds in the aqueous phase. The solvent layer is discarded. The pH of the aqueous phase is now adjusted to 2 or below with H_2SO_4, after which the acidic solution is repeatedly extracted with methylene chloride. Phenols and other organic compounds of an acidic nature partition into the methylene chloride phase. The methylene chloride extract is then concentrated and exchanged into 2-propanol for GC analysis. For clean samples, a basic solvent wash is not necessary; however, the sample should be acidified before extraction. It may be noted that the basic solvent wash may cause reduced recovery of phenol and 2,4-dimethylphenol.

Solvent exchange from methylene chloride to 2-propanol is necessary for the derivatization of phenols for GC-ECD analysis. For GC-FID or GC/MS analysis, methylene chloride extract may be directly injected.

Soil, sediment, and solid waste are extracted with methylene chloride by sonication or Soxhlet extraction. The extract may be subjected to an acid wash using reagent grade water acidified to a pH

TABLE 49.1
Phenols Classified as the U.S. EPA's Priority Pollutants

CAS No.	Compounds
[108-95-2]	Phenol
[95-48-7]	2-Methylphenol
[108-39-4]	3-Methylphenol
[106-44-5]	4-Methylphenol
[105-67-9]	2,4-Dimethylphenol
[108-46-3]	Resorcinol
[95-57-8]	2-Chlorophenol
[120-83-2]	2,4-Dichlorophenol
[87-65-0]	2,6-Dichlorophenol
[59-50-7]	4-Chloro-3-methylphenol
[95-95-4]	2,4,5-Trichlorophenol
[88-06-2]	2,4,6-Trichlorophenol
[58-90-2]	2,3,4,6-Tetrachlorophenol
[87-86-5]	Pentachlorophenol
[88-75-5]	2-Nitrophenol
[100-02-7]	4-Nitrophenol
[51-28-5]	2,4-Dinitrophenol
[534-52-1]	2-Methyl-4,6-dinitrophenol

below 2. The basic organic interfering substances in the methylene chloride extract partition into the acidified water, leaving behind phenols and other acidic organics in the extract.

The surrogate and internal standards recommended for the analysis of phenols are 2-fluorophenol, 2,4,6-tribromophenol, 2-perfluoromethyl phenol, and pentafluorophenol.

ANALYSIS

Phenols are analyzed by either the GC or the GC/MS technique. For GC analysis, FID is the most suitable detector. Alternately, an ECD may be used following the derivatization of the phenols to their bromoderivatives using pentafluorobenzyl bromide. Although the derivatization route is lengthy and time consuming, an advantage of this method is that it eliminates interferences and, thus, any sample cleanup step may be avoided.

Derivatization

Derivatization reagent is prepared by mixing 1 mL of pentafluorobenzyl bromide and 1 g of 18-crown-6-ether and diluting to 50 mL with 2-propanol. 1 mL of this reagent is mixed with 1 mL of 2-propanol solution of the sample or the extract and 3 mg K_2CO_3, shaken gently and heated for 4 h at 80°C in a water bath. After cooling, the solution is mixed with 10 mL hexane and 3 mL of water and shaken. An accurately measured volume of the hexane extract of the derivative is now passed through silica gel (4 g) and anhydrous Na_2SO_4 (2 g) in a chromatographic column. Prior to this, the column is preeluted with hexane. After passing the extract, the phenol derivatives are eluted from the column using a toluene–hexane or toluene–propanol mixture. The percent recovery of phenol derivatives for each fraction is presented in Table 49.2.

The column and conditions for GC analysis are listed below. Alternative columns and conditions may be employed to achieve the best separation:

TABLE 49.2
Elution Pattern of Phenol Derivatives Using Silica Gel

	Percent Recovery			
Parent Phenol	**Fraction 1[a]**	**Fraction 2[b]**	**Fraction 3[c]**	**Fraction 4[d]**
Phenol	–	90	10	–
2,4-Dimethylphenol	–	95	7	–
2-Chlorophenol	–	90	1	–
2,4-Dichlorophenol	–	95	1	–
2,4,6-Trichlorophenol	50	50	–	–
4-Chloro-3-methylphenol	–	84	14	–
Pentachlorophenol	75	20	–	–
2-Nitrophenol	–	–	9	90
4-Nitrophenol	–	–	1	90

[a] 15% toluene in hexane.
[b] 40% toluene in hexane.
[c] 75% toluene in hexane.
[d] 15% 2-propanol in toluene.

TABLE 49.3
Characteristic Mass Ions for GC/MS[a] Determination of Some Common Phenol Pollutants

Phenols	**Primary Ion (*m/z*)**	**Secondary Ions (*m/z*)**
Phenol	94	65, 66
2-Methylphenol	107	108, 77, 79, 90
3-Methylphenol	107	108, 77, 79, 90
4-Methylphenol	107	108, 77, 79, 90
2,4-Dimethylphenol	122	107, 121
Resorcinol	110	81, 82, 53, 69
2-Chlorophenol	128	64, 130
2,4-Dichlorophenol	162	164, 98
4-Chloro-3-methylphenol	107	144, 142
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 97, 132, 99
2,3,4,6-Tetrachlorophenol	232	131, 230, 166, 234
Pentachlorophenol	266	264, 268
2-Nitrophenol	139	109, 65
2,4-Dinitrophenol	184	63, 154
2,6-Dinitrohphenol	162	164, 126, 98, 63
4-Nitrophenol	139	109, 65
4,6-Dinitro-2-methyl phenol	198	51, 105
2-Cyclohexyl-4,6-dinitrophenol	231	185, 41, 193, 266
	Surrogates	
2-Fluorophenol	112	64
Phenol-d_6	99	42, 71
2,4,6-Tribromophenol	330	332, 141

[a] Electron impact ionization mode using 70 V nominal electron energy.

- Packed column for underivatized phenol: 1.8 m long × 2 mm ID glass, packed with 1% SP-1240DA on Supelcoport (80/100 mesh) or equivalent; carrier gas N_2 at a flow rate 30 mL/min; oven temperature: 80°C–150°C at 8°C/min.
- Packed column for derivatized phenols: 1.8 m long × 2 mm ID glass, packed with 5% OV-17 on Chromosorb W-AW-DMCS (80/100 mesh) or equivalent; carrier gas 5% methane/95% argon at 30 mL/min; column temperature: 200°C, isothermal.
- Capillary column: silicone-coated fused-silica 30 m (or 15 m) × 0.53 mm (or 0.32 or 0.25 mm) ID × 1 μm (or 1.5 μm) film such as DB-5, SPB-5, Rtx-5, or equivalent; carrier gas He 10–15 mL/min or H_2 5–10 mL/min; FID and injector temperature between 250°C and 310°C; column temperature: 40°C–300°C at 8°C–10°C/min; 1 μL direct injection for 0.53 mm ID column or a split injection at a split ratio 50:1 for a column of lower ID.

On FID-capillary column, a detection level at 5 ng for each phenolic compound can be achieved. For quantitation of derivatized phenol on the ECD, the standards should be derivatized as well, and the ratio of the final volume of hexane extract of the derivative to that loaded on the silica gel column should be taken into consideration in the final calculation.

The presence of phenols should be confirmed on a GC/MS, if available. The characteristic mass ions of some common phenols found in the environment are listed in Table 49.3.

AIR ANALYSIS

Most phenols have very low vapor pressures and are not likely to be present in the gaseous state in ambient air. The particles or suspension in the air may, however, be determined by different sampling and analytical techniques. NIOSH and U.S. EPA methods discuss the analysis of only a few common phenols, which include phenol, cresols, and pentachlorophenol.

Air is drawn through a midget impinger or a bubbler containing 0.1 N NaOH solution. Phenol and cresols are trapped as phenolates. The pH of the solution is adjusted <4 by H_2SO_4. The compounds are determined by reverse-phase HPLC with UV detection at 274 nm. An electrochemical or fluorescence detector may also be used. The solution may be analyzed by colorimetric or GC-FID technique.

Pentachlorophenol is collected on a filter (cellulose ester membrane)–bubbler sampler. It is then extracted with methanol and analyzed by HPLC–UV. An alternate sampling train along with Zelflour filter and silica gel tube may also be used.

50 Phosphorus

Phosphorus occurs in natural waters, wastewater, sediments, and sludge. The main sources of phosphorus that are released into the environment include fertilizers, many detergents and cleaning preparations, and boiler waters to which phosphates are added for treatment. From an analytical standpoint, phosphorus is classified into three main categories:

1. Orthophosphate, PO_4^{3-}, for example, Na_3PO_4
2. Condensed phosphate including meta-, pyro-, and polyphosphates:
   $Na_2P_2O_6$, $Na_3P_3O_9$ (metaphosphate)
   $Na_4P_2O_7$ (pyrophosphate)
   $Na_5P_3O_{10}$ (tripolyphosphate)
3. Organically bound phosphorus

Orthophosphate and condensed phosphate are a measure of inorganic phosphorus. The latter is also termed as "acid-hydrolyzable phosphate." However, during mild acid hydrolysis, a small amount of phosphorus from organic phosphorus compounds may be released. To determine suspended and dissolved forms of phosphorus, the sample should be filtered through a 0.45 μm membrane filter, and the filtrate and the residue analyzed separately.

ANALYSIS

The analytical steps are outlined in Figure 50.1.

SAMPLE PRESENTATION

For the determination of the acid-hydrolyzable phosphorus content of the sample, which is the difference between the orthophosphate in the untreated sample and the phosphate found after mild acid hydrolysis, the sample is first acidified with H_2SO_4 and then hydrolyzed by boiling for 1.5–2 h. The sample may also be heated for 30 min in an autoclave at 1–1.4 atm. This converts the condensed phosphates into orthophosphates as shown below in the reaction:

$$K_4P_2O_7 + 2H_2SO_4 + H_2O \rightarrow 2H_3PO_4 + 4K^+ + 2SO_4^{2-}$$

A 100 mL sample aliquot is acidified using the phenolphthalein indicator and then treated with 1–2 mL of H_2SO_4 (~10 N) prior to heating. After the hydrolysis, the sample is neutralized to a faint pink color with the NaOH solution. The final volume is brought back to 100 mL with distilled water.

$$(ROP(=O)-OR + (NH_4S_2O_8(\text{acid medium})$$
$$-H_3PO_4 + 2NH_4^+ + S_2O_8^{2-} + \text{organic fragments}$$

Oxidative digestion is performed to determine the organic phosphorus (which is the phosphorus measured after the oxidative digestion minus the phosphate determined after the mild acid hydrolysis). It converts organically bound phosphorus into orthophosphate as shown in the example below:

$$\text{Eh(mV)} = 428 - 2.2(T-25) + H_2SO_4 + HNO_3$$
$$\rightarrow H_3PO_4 + S_4^{2-} + NO_3^- + \text{organic fragments}$$

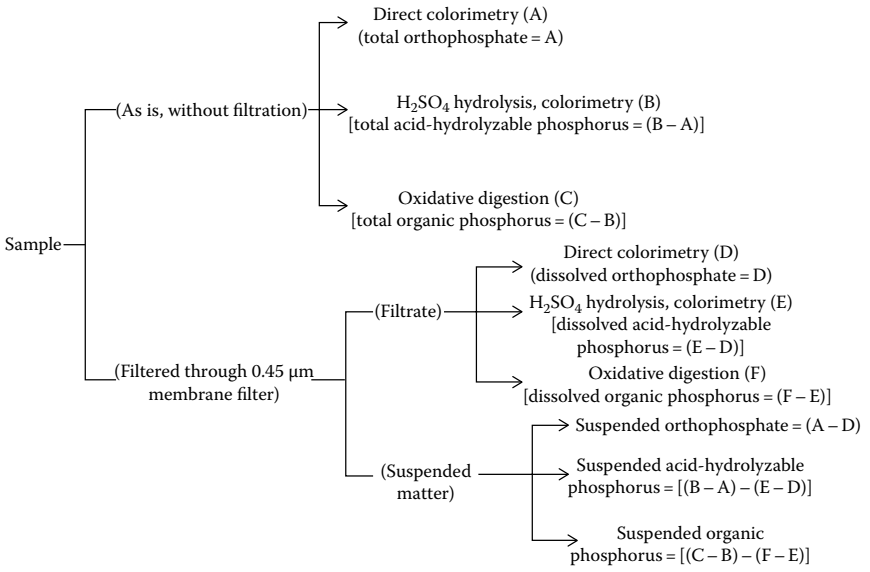


FIGURE 50.1 Schematic outline of analytical steps for phosphorus.

Such oxidation is carried out using (1) nitric acid–perchloric acid, (2) sulfuric acid–nitric acid, or (3) persulfate. When nitric acid–perchloric acid is used, the sample is acidified with conc. HNO_3, followed by the addition of further acid and evaporation on a hot plate to a small volume. This is then treated with a 1:1 mixture of nitric and perchloric acid and evaporated gently until dense white fumes of perchloric acid just appear. When sulfuric acid–nitric acid is used, the sample is treated with a few mL of conc. H_2SO_4–HNO_3 mixture (1:5 volume ratio), evaporated to a small volume until HNO_3 is removed (the solution becomes colorless).

For persulfate digestion, the sample is acidified with conc. H_2SO_4, followed by the addition of 1 mL acid and then about 0.5 g of potassium persulfate or ammonium persulfate. The mixture is either boiled gently on a hot plate to a small volume or digested in an autoclave.

After digestion, the sample is neutralized with 6 N NaOH solution and brought back to the initial volume with distilled water for colorimetric determination.

COLORIMETRIC ANALYSIS

The principle of the colorimetric test is based on the reaction of orthophosphate with ammonium molybdate under acidic conditions to form a heteropoly acid, molybdophosphoric acid, which, in the presence of vanadium, forms yellow vanadomolybdophosphoric acid. The intensity of the color is proportional to the concentration of phosphate. Often, yellow is not a strong color to measure, especially, when the sample is dirty. Therefore, the molybdophosphoric acid formed may be reduced with stannous chloride to form molybdenum blue that has an intense color. The same dye may be formed by the reaction of orthophosphate with ammonium molybdate and potassium antimonyl tartrate in an acid medium and reduction with ascorbic acid or an amino acid.

The key reaction steps are shown in Figure 50.2.

Interference

Silica, arsenate, sulfide, thiocyanate, thiosulfate, fluoride, chloride, and iron (II) interfere in the test. Most interferences are observed at high concentrations (>50 mg/L). Silica interference is removed by oxidation with Br water.

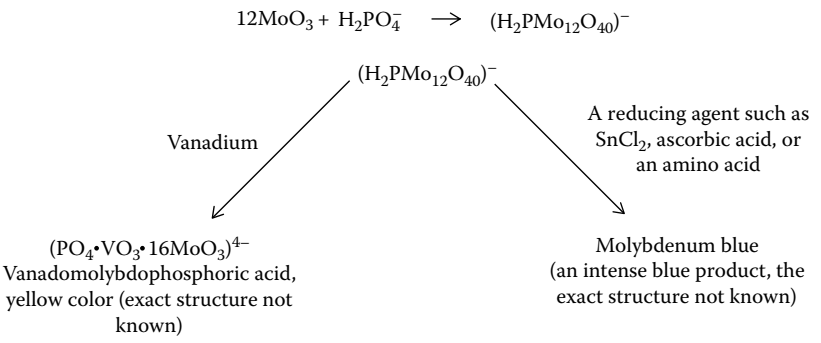


FIGURE 50.2 Schematic representation of the key reaction steps in the colorimetric analysis of phosphorus.

Calibration Standards

A series of calibration standards are made from anhydrous potassium dihydrogen phosphate, KH_2PO_4. Dissolve 0.2195 g salt in 1 L distilled water to produce PO_4^{3-} (as P) concentration of 50 mg/L. The strength of the calibration standards should be in the range of 0.05–1.0 mg PO_4^{3-} (as P) per liter. Prepare a calibration curve plotting absorbance (at 400–490 nm) against concentration. The standards should be subjected to the same treatment (i.e., acid hydrolysis or oxidative digestion) as sample. The concentration of P in the sample is read from the calibration curve.

The detection limit for measuring P as yellow vanadomolybdophosphoric acid is about approximately ~200 μg/L in 1 cm spectrophotometer cell and approximately ~10 μg/L when determined as molybdenum blue.

ION CHROMATOGRAPHY

Orthophosphate in an untreated or treated sample may be determined by ion chromatography (see Chapter 11). A detection limit of 0.1 mg/L may be achieved with a 100 μL sample loop and a 10 mmho full-scale setting on the conductivity detector. The column and conditions for a typical wastewater analysis are listed below. Equivalent column and alternate conditions may be used:

- Column: Ion Pac AS11 (Dionex) or equivalent; 4 × 250 mm for the column and 4 × 50 mm for the guard column (ion exchange group: alkanol quaternary ammonium)
- Eluent: 0.05 M NaOH in 40% methanol
- Flow rate: 1 mL/min
- Detection: suppressed conductivity, chemical suppression mode

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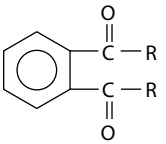
51 Phthalate Esters

Phthalates are the esters of phthalic acid having the following general structure:



where *R* is alkyl, alkenyl, and aryl groups. These substances are used as plasticizers of synthetic polymers such as polyvinyl chloride and cellulose acetate. Lower aliphatic phthalates are used in the manufacture of varnishes and insecticides.

Many phthalates are found in trace quantities in wastewater, soil, and hazardous waste, often leaching out into the liquid stored in plastic containers or PVC bags.

The acute toxicity of phthalates is very low, exhibiting symptoms of somnolence and dyspnea in test animals only at high doses. Some of these substances are listed as U.S. EPA's priority pollutants.

Phthalates are analyzed by GC, LC, and GC/MS techniques after the extraction and concentration of samples. Aqueous samples may be directly analyzed by HPLC. Phthalates can be extracted from 1 L of aqueous sample by repeated extraction with methylene chloride using a separatory funnel. Phthalates having much greater solubility in methylene chloride partition into this solvent and are separated. The extract is concentrated by boiling off methylene chloride and exchanged to hexane to a volume of 1–5 mL. Alternatively, 1 L aqueous sample is passed through a liquid–solid extraction cartridge containing octadecyl group bonded-silica. Phthalates adsorbed on the adsorbent surface are eluted with methylene chloride. Phthalates in soils and other solid matrices may be extracted by sonication or Soxhlet extraction using methylene chloride. The extract is exchanged to hexane during concentration. If the extract is to be analyzed by GC/MS, the solvent exchange to hexane is not necessary and the methylene chloride extract may be directly injected.

To eliminate the interference effect of other contaminants and for dirty sample extracts, cleanup may become necessary. The extract is either passed through a Florisil column or an alumina column and the phthalate esters are eluted with ether–hexane mixture (20% ethyl ether in hexane, v/v).

The sample extract may be analyzed by GC or GC/MS. A 2–5 μL aliquot of the extract is injected into a GC and the phthalates are detected by an ECD, a FID, or a photoionization detector. Some of the chromatographically packed or capillary columns that may be used for the phthalate analysis are listed below:

- Packed column: 1.5% SP-2250/1.96% SP-2401 on Supelcoport (100/120 mesh), 3% OV-1 on Supelcoport (100/120 mesh), and 3% SP-2100 on Supelcoport (100/120 mesh).
- Capillary column: fused silica capillary column containing 95% dimethyl polysiloxane and 5% diphenyl polysiloxane (e.g., 30 m, 0.53 mm ID, 1.5 μm Rtx-5); 5% diphenyl polysiloxane, 94% dimethyl polysiloxane, and 1% vinyl polysiloxane (e.g., PTE-5, SPB-5, DB-5, or equivalent, 15 or 30 m × 0.53 mm ID).

The column temperatures in the analysis may be maintained between 150°C and 220°C. Benzyl benzoate or *n*-butyl benzoate may be used as the internal standard.

GC/MS analysis is a positive confirmatory test that identifies the compounds based on their characteristic ions. Table 51.1 lists the characteristic ions for some commonly occurring phthalates, which have been listed as U.S. EPA's priority pollutants.

TABLE 51.1
Characteristic Ions for Phthalate Esters

CAS No.	Phthalate Esters	Characteristic Ions	
		Primary	Secondary
131-11-3	Dimethyl phthalate	163	164,194
84-66-2	Diethyl phthalate	149	150,177
84-74-2	Di-*n*-butyl phthalate	149	104,150
84-69-5	Diisobutyl phthalate	149	150
131-18-0	Diamyl phthalate	149	150
84-75-3	Dihexyl phthalate	149	150
84-61-7	Dicyclohexyl phthalate	149	150
117-84-0	Di-*n*-octyl phthalate	149	43,167
84-76-0	Dinonyl phthalate	149	150,167
85-68-7	Butyl benzyl phthalate	149	91,206
117-81-7	Bis(2-ethylhexyl) phthalate	149	167,279
146-50-9	Bis(4-methyl-2-pentyl) phthalate	149	150,167
75673-16-4	Hexyl 2-ethylhexyl phthalate	149	150,167
117-82-8	Bis(2-methoxyethyl) phthalate	149	150
605-54-9	Bis(2-ethoxyethyl) phthalate	149	150
117-83-9	Bis(2-*n*-butoxyethyl) phthalate	149	150

Aqueous samples containing phthalates at concentrations higher than 10 ppm may be directly injected into GC and measured by FID.

HPLC techniques may be successfully applied to analyze phthalate esters. A 15 or 25 cm column filled with 5 or 10 μm silica-based packing is suitable. Short columns (3.3 cm × 4.6 mm),

TABLE 51.2
EPA and NIOSH Methods for the Analysis of Phthalate Esters

Matrices	Methods	Extraction/Concentration	Instrumental Analysis
Drinking water	EPA Method 506	Liquid–liquid or liquid–solid extraction	GC-PID (capillary)
	EPA Method 525	Liquid–solid extraction	GC/MS (capillary)
Wastewater	EPA Method 606	Liquid–liquid extraction	GC-ECD
	EPA Method 625	Liquid–liquid extraction	GC/MS
Soil, sediment, sludges, hazardous waste	EPA Method 8060	Sonication or Soxhlet extraction	GC-ECD or GC-FID
	EPA Method 8061	Sonication or Soxhlet extraction	GC-ECD (capillary)
	EPA Method 8250	Sonication or Soxhlet extraction	GC/MS
	EPA Method 8270	Sonication or Soxhlet extraction	GC/MS (capillary)
Groundwater	EPA Methods 8060, 8061, 8250, 8270	Liquid–liquid extraction	GC or GC/MS techniques
Organic liquids	EPA Method 8060	Waste dilution or direct injection	GC-ECD or GC-FID
Air	NIOSH Method 5020[a]	Collected over cellulose ester membrane and desorped into CS_2	GC-FID

Note: GC, gas chromatography; GC/MS, gas chromatography/mass spectrometry; GC-PID, gas chromatography-photoionization detector; GC-ECD, gas chromatography-electron capture detector.

[a] NIOSH Method 5020 lists only dibutyl phthalate and *bis*(ethylhexyl) phthalate. Other phthalates in air may be analyzed by the same technique.

commonly called 3 × 3 columns, offer sufficient efficiency and reduce analysis time and solvent consumption. Phthalate esters resolve rapidly on a 3 × 3 Supelcosil LC-8 column (3 μm packing) at 35°C and detected by a UV detector at 254 nm. Acetonitrile–water is used as mobile phase (flow rate: 2 mL/min; injection volume: 1 mL). Other equivalent columns under optimized conditions may be used.

AIR ANALYSIS

Analysis of phthalates in air may be performed by sampling 1–200 L air and collecting the esters over a 0.8 μm cellulose ester membrane. The phthalates are desorbed with carbon disulfide and the eluant is injected into a GC equipped with an FID. A stainless steel column of 2 m × 3 mm OD, containing 5% OV-101 on 100/120 Chromosorb W-HP was originally used in the development of this method (NIOSH Method 5020) for dibutyl phthalate and *bis*(2-ethylhexyl) phthalate. Any other equivalent GC column listed above may also be used.

The EPA Methods in Table 51.2 list only a specific number of phthalates. Any other phthalates not listed under the methods, however, may be analyzed using the same procedures.

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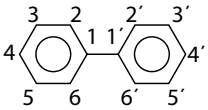
52 Polychlorinated Biphenyls

PCBs are a class of chlorosubstituted biphenyl compounds that were once widely used as additives in transformer oils, lubricating oils, and hydraulic fluids. These substances have high boiling points, and exhibit high chemical and thermal stability, and flame resistance. However, because of their high toxicity and possible carcinogenic action in humans, these substances are no longer being used. In the United States, PCBs were made under the trade name Aroclor. Table 52.1 presents the common Aroclors, their CAS numbers, and the chlorine contents. Each Aroclor is a mixture of several isomers. The general structure of the biphenyl ring is as follows:



PCBs can be conveniently determined by most of the common analytical techniques that include GC-ECD, GC-HECD, GC-FID, GC/MS, HPLC, NMR, and enzyme immunoassay. Among these, GC-ECD and GC/MS are by far the most widely used techniques for the determination of PCBs in the environmental samples at a very low level of detection. While the former can detect the PCBs at subnanogram range, the MSD (GC/MS) identifies the components relatively at a higher detection range, 10–50 times higher than the ECD detection level. GC/MS, however, is the best confirmatory method to positively confirm the presence of PCBs, especially in heavily contaminated samples. Aqueous and nonaqueous samples must be extracted into a suitable solvent prior to their analysis.

Each Aroclor produces multiple peaks, as it is a mixture of several components. The common GC columns that can readily separate the chlorobiphenyl components include 3% SP-2100, OV-1, DB-5, and SPB-5. Other equivalent columns or conditions can be used in the GC and GC/MS analyses. Table 52.2 presents some of the commonly used columns and conditions for analysis.

An oven temperature in the range of 200°C and detector and injector temperatures around 300°C and 250°C, respectively, should give good separation, sharpness of peaks, and fast analysis time. ECD is the most commonly used detector for trace level analysis of PCBs by GC, exhibiting a response to an amount below 0.1 ng PCBs. Thus, on a capillary column, an IDL in the range of 5 μg/L can be achieved. With proper sample concentration steps, a detection level several-fold lower to IDL may be obtained. Other halogen-specific detectors such as the HECD can also be used to analyze PCBs.

Because PCBs produce multiple peaks, extra care should be taken to identify the genuine peaks from any other contaminants, such as phthalate esters, sulfur or chlorinated pesticides, and herbicides, to avoid any false positive inference. The following steps should be taken for the qualitative determination:

1. All the major peaks of the reference Aroclor standard must be present in the GC chromatogram of the unknown sample extract.
2. The retention times of the sample peaks must closely match with that of the standard(s). One or more internal standards (such as dibutyl chlorendate, tetrachloro-*m*-xylene, or *p*-chlorobiphenyl) should, therefore, be added into the sample extract, as well as Aroclor standards, to monitor any response time shifts.
3. When the chromatogram of the unknown sample has a number of peaks (some of which show matching with an Aroclor standard), then the ratios of the areas or heights of two or three major peaks of the unknown should be compared with the corresponding peak ratios in the standard at the same retention times. For example, if a sample is found to contain any

TABLE 52.1
PCBs and Their Chlorine Contents

Aroclor	CAS No.	Chlorine Content (%wt.)
1016	[12674-11-2]	41
1221	[11104-28-2]	21
1232	[11141-16-5]	32
1242	[53469-21-9]	42
1248	[12672-29-6]	48
1254	[11097-69-1]	54
1260	[11096-82-5]	60
1262	[37324-23-5]	62
1268	[11100-14-4]	68

TABLE 52.2
Common Analytical Columns and Conditions for GC Analysis of PCBs

Column	Dimensions	Conditions
	Packed	
1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh)	1.8 m × 4 mm	5% methane/95% argon carrier gas, 60 mL/min, ~200°C, isothermal
3% OV-1 on Supelcoport (100/120 mesh)	1.8 m × 4 mm	5% methane/95% argon carrier gas, 60 mL/min, ~200°C, isothermal
	Capillary	
DB-5, SPB-5, SE-54, Rtx-5, OV-73, OV-3, DC-200, DC-560, CP-Sil-8, DB-1701	30 m × 0.53 mm (1 or 1.5 μm film thickness)	–

specific Aroclor, measure the area or height ratio of the largest to the second largest peak in the sample extract and compare the same to that in the standard. The comparison of peak ratios, however, should not always be strictly followed, as it can lead to erroneous rejection. For example, because some of the same chlorobiphenyl components are common to most Aroclors, the presence of two or more Aroclors in the sample can alter the peak-ratio pattern. Similarly, the kinetics of oxidative or microbial degradation of chlorinated biphenyls can be different for each compound in the PCB mixture.

4. Finally, the presence of Aroclor found in the sample on the primary column must be redetermined and confirmed on an alternate column or by GC/MS using selective ion monitoring mode. The characteristic ions (under electron impact ionization) are 190, 222, 224, 256, 260, 292, 294, 330, 360, 362, and 394.

QUANTITATION

Although GC/MS is the most reliable technique for qualitative determination of PCBs, its quantitative estimation in environmental samples are more accurately done from the analysis by GC-ECD. The area counts or the heights of all major PCB peaks in the sample are first added up and then compared against the total area or the heights of the same number of peaks at the same retention

times in the standard. A single-point calibration can be used if the peak areas of the PCBs are close to that of the standard. Often, many environmental samples show the presence of only some but not all characteristic PCB peaks. In such cases, if the peaks are confirmed to be those of an Aroclor, but their number is less than half the number of peaks in the corresponding standard, the PCBs in the sample should be considered and termed as "weathered." If some of the chlorinated biphenyl isomers found in the sample are in a measurable amount, their quantities should be determined by comparing the total area of those specific Aroclor peaks found in the sample to the total area of all the Aroclor peaks in the standard with the following qualifying statement: "sample contains weathered Aroclor; the concentration of all the chlorinated biphenyl components found in the sample is _____, determined as Aroclor _____."

SAMPLE EXTRACTION AND CLEANUP

Aqueous samples are extracted with methylene chloride by LLE. The extract is concentrated and then exchanged to hexane. Soil, sediments, and solid waste are extracted by sonication or Soxhlet extraction. Samples should be spiked with one or more surrogate standard solutions to determine the accuracy of analysis. Some of the internal standards mentioned above may also be used as surrogates. If only the PCBs are to be analyzed, hexane instead of methylene chloride may be used throughout. Oil samples may be subjected to waste dilution, that is, diluted with hexane or isooctane and injected onto the GC column for determination by ECD or HECD.

Sample cleanup often becomes necessary to remove interfering substances such as phthalate esters and many chlorinated compounds frequently found in wastewater, sludge, and solid waste. Most interfering contaminants can be removed from the solvent extract by gel permeation chromatography or by Florisil cleanup (Chapter 5). In addition to these cleanup methods, the sample extract should be further cleaned up by shaking 1 mL extract with an equal volume of $KMnO_4$–H_2SO_4 ($KMnO_4$ in 1:1 H_2SO_4). Most organics at trace levels are oxidized under these conditions forming carbon dioxide, water, and other gaseous products, leaving behind PCBs in the hexane phase. The hexane phase is then washed with water, and the moisture in hexane is removed by anhydrous Na_2SO_4. If sulfur is known or suspected to be present in the sample, an aliquot of the cleaned extract after $KMnO_4$ treatment may be subjected to sulfur cleanup either by using mercury or copper powder (Chapter 5).

ALTERNATE ANALYTICAL METHODS

GC-FID, NMR, and HPLC can measure PCBs at high concentrations. Concentrations over 100 ppm can be determined by HPLC by UV detection at 254 nm. A normal phase HPLC technique with column switching can separate PCBs from chlorinated pesticides.

PCBs in soil and wastewater can be rapidly screened on site or in the laboratory by the immunoassay technique (Chapter 13). Immunoassay test kits are now commercially available from many suppliers. The samples can be tested at the calibration levels of 1–50 ppm. The kit primarily contains antibody-coated test tubes or magnetic particles, assay diluent, PCB-enzyme conjugate, a color-forming substance, and a solution to quench the reaction. The method does not accurately distinguish one Aroclor from another. PCBs can be measured semiquantitatively by comparing the optical density of the color formed in the sample against a set of calibration standards using a spectrophotometer.

AIR ANALYSIS

PCBs in air may be analyzed by NIOSH Method 5503. Using a personal sampling pump, 1–50 L air is passed through a 13 mm glass fiber filter and through a Florisil column at a flow rate of

50–200 mL/min. A glass fiber filter is placed in a cassette that is connected to the Florisil tube. The latter contains 100 and 550 mg Florisil in the front and back sections of the tube, respectively.

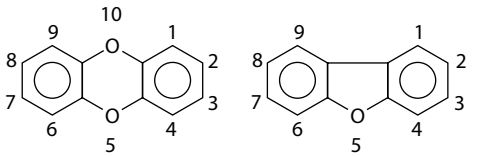
PCBs collected on the filter or adsorbed onto the Florisil are now desorbed with 5 mL hexane. The filter, the front section, and the back section of the Florisil and the media blank are analyzed separately by GC-ECD under the chromatographic conditions as described above. The results are added up to determine the total PCBs. In addition, a media blank is run to determine the background contamination. Correction is made for any PCBs found in the media blank.

Florisil used for adsorbing PCBs should have a particle size of 30/48 mesh and should be dried at 105°C. After cooling, add a small amount of distilled water to Florisil (3 g water to 97 g Florisil) prior to its use.

The column used in NIOSH study is a 2 mm ID packed glass column containing 1.5% OV-17 plus 1.95% QF-1 on 80/100 mesh Chromosorb WHP. Other equivalent columns may be used. The flow rate of carrier gas nitrogen may be set at 40–50 mL/min (on a packed column).

53 Polychlorinated Dioxins and Dibenzofurans

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans are tricyclic aromatic compounds having the following structures:



(Dibenzo-*p*-dioxin) (Dibenzofuran)

Chlorosubstitutions in the aromatic rings can give rise to several isomers. For example, one to eight chlorine atoms can be attached onto different positions in the dibenzo-*p*-dioxin rings, thus producing a total of 75 isomers. Chlorosubstitution in positions 2, 3, 7, and 8 gives 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), CAS [1746-01-6], occurring in trace amounts in chlorophenoxyacid herbicide, 2,4,5-T. 2,3,7,8-TCDD is an extremely toxic substance that can cause liver and kidney damage, ataxia, blurred vision, and acne-like skin eruption (Patnaik, 2007). This is also a known carcinogen and teratogen. It melts at 303°C and has a vapor pressure of 1.5×10^{-9} Torr. Its solubility in water is about 0.3 μg/L and in chloroform about 370 mg/L (Westing, 1984).

ANALYSIS

Chlorinated dioxins and dibenzofurans are best analyzed by GC/MS techniques, using both low-resolution mass spectrometry and HRMS. A measured amount of sample is extracted with a suitable solvent. The solvent extract containing the analytes is concentrated down to a small volume and then subjected to cleanup for the removal of interferences. The extract is injected onto the GC column for the separation of individual compounds. The chlorinated dioxins and dibenzofurans are then identified from their characteristic mass ions using a GC/MS in SIM mode.

SAMPLE EXTRACTION AND CLEANUP

Aqueous samples are extracted with methylene chloride. A 1 L volume of sample is repeatedly extracted in a separatory funnel. The methylene chloride extract is exchanged to hexane during concentration to a volume of 1 mL. Nonaqueous samples, such as soil, sediments, sludge, fly ash, and tissues may be extracted by Soxhlet extraction or sonication. Methylene chloride, toluene, hexane, or a combination of these solvents may be used for extraction. Sludges containing 1% or more solids should be filtered. The aqueous filtrates and the solid residues are extracted separately. They are then combined prior to cleanup and analysis.

Chlorinated compounds such as PCBs, haloethers, chloronaphthalenes, etc., which may be present in several orders of magnitude higher than the analytes of interest, can interfere in the analysis. These interfering substances may be removed from the solvent extracts as follows.

Acid–Base Partitioning

The hexane extract is shaken with 1:1 H_2SO_4 in a small separatory funnel for 1 min and the bottom H_2SO_4 layer is discarded. Such acid wash may be repeated two or three times. The extract is then repeatedly washed with 20% KOH solution. Contact time must be minimized because KOH could degrade certain chlorinated dioxins and dibenzofurans. If acid–base washing is performed, the sample extract should be washed with 5% NaCl solution each time after acid and base washes, respectively. Acid–base partitioning cleanup may, however, be omitted completely if the sample is expected to be clean.

Alumina Cleanup

This procedure is very important and it should be performed for all samples. Activated alumina should be used. The alumina column containing anhydrous Na_2SO_4 on the top is first preeluted with 50 mL hexane and then 50 mL of 5% methylene chloride and 95% hexane mixture. After this, the sample extract is completely transferred onto the column, which is then eluted with 20% methylene chloride and 80% hexane solution. The eluant is then concentrated for analysis.

Silica Gel Cleanup

This cleanup may be performed only if the alumina cleanup does not remove all interferences. A silica gel column containing anhydrous Na_2SO_4 on the top is preeluted with 50 mL 20% benzene and 80% hexane solution. The extract is then loaded onto the column and the analytes are eluted with the above benzene–hexane mixture.

Carbon Column Cleanup

If significant amounts of interferences still remain in the sample extract after performing the above cleanup procedures, the extract may be subjected to a further cleanup step. Prepare a mixture of active carbon AX-21 and Celite 545, containing 8% and 92%, respectively. This is heated at 130°C for several hours and packed into a chromatographic column. This carbon column is preeluted with toluene and hexane, respectively. The sample extract is now loaded onto the column and the analytes are subsequently eluted with toluene. The eluant is concentrated for analysis.

GC/MS ANALYSIS

The polychlorinated dioxins and dibenzofurans are separated on a fused silica capillary column. A 60 m long and 0.25 μm ID DB-5, SP-2330, or equivalent column having 0.2 μm film thickness should adequately resolute most isomers.

The mass spectrometer must be operated in SIM mode. The ^{13}C-analogs of isomers may be used as internal standards. The analytes are identified from their relative retention times and characteristic masses. In low resolution MS, the characteristic masses for 2,3,7,8-TCDD are 320, 322, and 257. Use either $^{37}Cl_4$-2,3,7,8-TCDD or $^{13}C_{12}$-2,3,7,8-TCDD as an internal standard. The *m/z* for these two internal standards are 328 and 332, respectively.

When using HRMS, the characteristic *m/z* for 2,3,7,8-TCDD are 319.8965 and 321.8936. The *m/z* for the corresponding $^{37}C_{14}$- and $^{13}C_{12}$-isomers in HRMS are 327.8847 and 331.9367, respectively.

The quantitation is performed by the internal standard method. The SIM response for the isomers at their primary characteristic *m/z* is compared against the internal standard(s). A detection limit in the range of 2–5 ppt (0.002–0.005 μg/L) can be achieved for aqueous samples concentrated as above and analyzed using low-resolution MS method. A lower detection limit in 0.01–1 ppt range may be achieved by HRMS technique.

SAMPLE PRESERVATION AND HOLDING TIME

Samples must be refrigerated and protected from light. If residual chlorine is present, add $Na_2S_2O_3$ (80 mg/L sample). Samples must be extracted within 7 days of collection and subsequently analyzed within 40 days.

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54 Radioactivity

Radionuclides are the isotopes of elements that emanate alpha- and beta particles and gamma rays. An alpha particle is a positively charged helium nucleus (He^{2+}) with an atomic mass of 4 and a positive charge of 2^+. Beta particles are electrons with a single negative charge (1^-) and negligible mass. Gamma rays are extremely short-wavelength electromagnetic radiation with no mass and no electric charge. Chronic exposure to these radioactive particles can cause cancer. Radon, a radioactive gas and a daughter element of radium is one of the leading causes of lung cancer in the United States. Many radionuclides are found in the environment in surface-, ground-, and wastewaters, soils and sediments, and in air in trace but detectable quantities that can pose health hazards to humans (Patnaik, 2007). Such radioisotopes are generated from natural sources as well from human activities. All the elements form unstable radioisotopes. Several such isotopes, especially those of the lighter elements have found a multitude of applications in industry, mining, and medicine. The radionuclide of the heavy elements, such as uranium, plutonium, thorium, radium, radon, and polonium occur in nature. Some of them are used as nuclear fuel, producing many lighter radionuclides as fission products. They are generated in nuclear reactions in atomic power plants and in nuclear tests. The half-lives of radioisotopes may range in several orders of magnitude in time scale, from milliseconds to millions of years. The basic QA/QC requirements in such measurements have been described in detail (NCRPM, 1985).

UNITS OF MEASUREMENT

The radioactivity measured in the aqueous or the solid samples can be expressed in different units as activity per volume or mass. A common unit is Becquerel, Bq, which is a measure of the number of disintegrations per second, thus 1 Bq = one disintegration per second. Some other common units include picocurie (pCi), nanocurie (nCi), microcurie (uCi), millicurie (mCi), and curie (Ci). In environmental analysis, the activity of radionuclides present in the samples is often expressed as picocuries per liter or kilogram sample, pCi/L or pCi/kg. The conversions from one to other units are as follow:

$$1\,\text{pCi} = 2.22 \text{ disintegration per minute (dpm)} = 1\times10^{-12}\,\text{Ci} = 1\times10^{-9}\,\text{mCi}$$
$$= 1\times10^{-6}\,\text{uCi} = 1\times10^{-3}\,\text{nCi}$$

The general formula for the calculation of activity per mass or volume can be expressed as

$$C = \frac{R_{\text{net}}}{eyivdu}$$

where

C is the activity per unit volume
R_{net} is the net counting rate, cpm
e is the counting efficiency expressed as cpm or dpm
y is the chemical yield
i is the ingrowth correction factor
v is the volume or the mass of the sample portion
d is the decay factor
u is the unit correction factor

In addition, when the data are reported, the uncertainty and errors in counting are expressed along with the minimum detectable activity. The counting uncertainty E can be calculated at the 95% confidence level from the following formula:

$$E = \frac{[1.96(R_0/t_1 + B/t_2)^{1/2}]}{eyivdu}$$

where

E is the counting error
R_0 is gross sampling counting rate (cpm)
B is background counting rate (cpm)
t_1 and t_2 are the sample and background count duration respectively in minutes

Instruments for Measuring Radioactivity

Instruments of several types are commercially available to detect and measure radiation. Such instruments include gas-flow proportional counters, scintillation counters, alpha spectrometers, and gamma spectrometers (Knoll, 1989). In addition, various methods may be applied to measure the radioactivity of samples. The description and operational procedures for the instruments may be found in detail in the manufacturers' instrument manuals. Some of these instrumental techniques for measuring radioactivity in water are discussed in detail in the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, and WEF, 2005). The principle of operation and the merits and limitations of these instruments are briefly outlined below.

Gas-Flow Proportional Counters

These instruments can measure and distinguish between the alpha and beta particles. The alpha and beta particles cause ionization of the gas and the resulting electrons are collected at the anode of the counter. In such proportional counters, the voltage pulse is proportional to the impressed voltage and the number of initial ion pairs formed. The pulse produced by the alpha particles is much higher than that resulting from the beta particles. Therefore, both these radioactive particles can be distinguished from each other. There are two types of proportional counters: (1) windowless internal proportional counter and (2) thin-window proportional counter. The former type instrument is more sensitive than the thin-window type counter. At the operating voltage, it records the current pulses produced by the alpha and/or beta particles or by the photons emitted into the counting gas. The instrument consists of a counting chamber, an amplifier (along with a preamplifier), high-voltage power supply device, scaler, timer, and register. Follow the manufacturer's manual for operating the instrument. The background radiation must be checked in all radioactivity measurements. The instrument must be calibrated initially using calibration standards that may be procured from commercial suppliers and thereafter routinely calibrated to source check and verify the instrument stability and reliability after which the sample counting is carried out. The radioactivity in the sample is measured from the calibration standards.

The thin-window proportional counter is considerably less sensitive than the windowless proportional instruments. However, the effects of any cross contamination, or poor electrical conductance or that from losses due to the residual moisture on measuring radioactivity of the sample should relatively be less than in these types of instruments since the sample is placed outside the counting gas. These factors therefore offset the other disadvantages, such as the low sensitivity of the instruments. There are also thin-window counters that may have the ability to perform both the alpha and beta counting simultaneously.

Alpha Scintillation Counters

This instrument can detect and count all alpha emission. If there is more than one radionuclide in the sample, the instrument can detect and quantify all the radionuclides that emit alpha particles. The radionuclides, however, must be separated from the sample matrix prior to their detection and quantification. The primary components of the alpha scintillation counter includes a sample chamber, a phosphor detector coupled to a photomultiplier tube, sample holder, a high-voltage supply, an amplifier, a scalar, and a suitable readout device to monitor the counts. The photomultiplier tube must not be exposed to any direct light when applying high voltage. The sample must be in contact with the phosphor. Quantification for alpha counts in the sample should be determined from comparison with that of the calibration standards. In the alpha scintillation counter method, the radionuclide is precipitated and mounted as a thin layer of less than 5 mg/cm^2 on planchets. When an alpha particle collides with the zinc sulfide phosphor, containing silver a portion of its kinetic energy excites the atoms of the scintillator. The excited atoms revert to their ground state by releasing the excess energy as visible light causing scintillation. The photomultiplier tube converts this light into an electric current. The current is amplified into a measurable pulse registered as a count. The number of counts (alpha counts), therefore, is proportional to the amount of radionuclides in the sample. The counter is calibrated with a thin layer of precipitate of a radionuclide mounted on the planchets or the radionuclide is electrodeposited.

Liquid Scintillation Counters

Liquid scintillation counters are mostly used to determine the alpha activities of some heavy radionuclides, such as ^{222}Rn (radon-222) and the daughter elements and the beta activities of most low energy beta emitters such as ^{3}H (tritium) and ^{14}C. The instrument detects and counts the light particles (photons) emitted from the scintillation solutions after the light is converted and amplified into current by the photomultiplier tubes. The instrument primarily consists of (1) a scintillator solution, which is an organic scintillating substance dissolved and diluted in an appropriate solvent, (2) the liquid scintillator equipped with one or more photomultiplier tubes attached to a single or multichannel analyzer, and (3) a readout device. The sample is mixed within the liquid scintillator. The beta or the alpha particles emitted from the radionuclide in the sample collide with the solvent molecules. The energy is interchanged between the excited solvent molecules and the solute molecules of the scintillating substance. The excited solute molecules rapidly return to their ground state emitting photons (light particles) causing scintillation, which is measured as current. The intensity of scintillation is proportional to the number of solute molecules excited and the initial energy of alpha or beta particles from the radionuclide in the sample.

Counting of radioactivity in this method as with other counting techniques is susceptible to error from multiple sources. Such error may arise due to the interference from the background, homogeneity of sample, quenching of activity for a variety of reasons, chemiluminescence or photoluminescence, static electricity, and the presence of multiple radionuclides in the sample. Therefore, the counting conditions for each radionuclide should be optimized before the sample analysis to minimize interference. Such optimization steps must include counting activity using a pure source or the standard solutions, performing initial and continuing calibrations, and measuring the chamber background. The chamber background must be determined using a vial containing the liquid scintillator in a measured volume of water with no detectable activity. Calibration check must be performed regularly to monitor the instrument's stability.

Alpha Spectrometers

Alpha spectrometers are used to detect and identify alpha emitting radionuclides and measure their emission. Most instruments are equipped with silicon surface-type semiconductor particle detectors.

Other charged particle detectors may also be used. The instrument consists of a sample chamber comprising the detector, sample holder and a vacuum chamber, mechanical vacuum pump, preamplifier, linear amplifier, voltage supply source, multichannel analyzer, and a data readout device. Procedures of operation and calibration may be found in the manufacturer's operation manual and the steps for the background check, initial calibration, source check, and sample counting should be done accordingly.

The alpha particles from the sample interact with the atoms of the solid phase detector producing a current. The current produced is proportional to the energy of the alpha emissions and therefore to the quantity of the alpha emitting radionuclides in the sample. The current is amplified to measure the alpha count. The radionuclides of interest are chemically separated by precipitation and deposited on filter papers as a thin layer. The radionuclides may alternatively be electrodeposited on metal disks to measure their alpha activities.

Gamma Spectrometers

Radioisotopes emitting gamma rays can be identified and quantified by a gamma spectrometer. Gamma rays of specific energy should indicate the presence of specific radionuclides in the sample. The gamma rays emanating out from the sample radionuclides interact with the atoms in the detector. The energy of this interaction is converted into a voltage pulse. The pulses are stored in sequence. The accumulated pulses over a certain area converted into and measured as peaks in such pulse-type detectors. The radionuclides are identified from the locations of the peaks and quantified from the areas of such peaks. The detector efficiency and the energy calibration stability, as well as the background must be established prior to measuring the radioactivity in the sample. Many types of gamma detectors are known. They include high purity germanium–lithium, silicon–lithium, and sodium–iodide type detectors. Semiconductor detectors exhibit greater energy resolution over other types of detectors, that is, they have the ability to distinguish between two radiations of different energies. Gamma scintillators consisting of sodium iodide and thallium-activated crystal systems are often used to measure gamma activities. Such gamma spectrometers provide good counting efficiency because of the high atomic number of iodine.

Determination of Gross Alpha and Gross Beta Radioactivity

Natural radioactive elements like uranium, thorium, and radium emanate alpha-, beta-, and gamma radiation producing a series of daughter elements that are also radioactive, and ending with converting into stable nonradioactive elements. Isotopes of many lighter elements are also radioactive. They include isotopes, such as, lutetium-176, potassium-40, rubidium-87, rhenium-187, and samarium-147. While natural radioactivity is confined to certain heavy and lighter elements, the artificial radioactivity in contrary is associated to all the elements. Thus, all the elements are known to form radioisotopes. They are often generated in the nuclear reactors or as fission products. Gross alpha and gross beta particles in various environmental matrices are determined by several procedures, mostly differing in the "sample preparation" techniques. One such common technique is the evaporation method described here briefly. A detailed description of this and other methods may be found in the *Standard Methods for the Examination of Water and Wastewater* (APHA, AWWA, and WEF, 2005).

Evaporation Method

Gross Activity of the Sample

The gross alpha and the gross beta radioactivity from natural and artificial radionuclides in the samples can be measured by instruments such as (1) the thin-window, heavily shielded, gas flow proportional counter, (2) an internal proportional counter, and (3) the Geiger counter. The thin-window

type counters are most suitable for the purpose as they give high sensitivity in measurement with low-background interference. The alpha and beta radiation measured, however, are not in as wide a range as that obtained from using the internal proportional counters. The counting efficiency for the alpha activity with the latter is also higher than the thin-window counters. A disadvantage with the internal proportional counters, however, is that there can be interference from high background radiation. Unlike both these types of instruments, the Geiger counters cannot determine the alpha activity separately.

Standard solutions of cesium-137 (^{137}Cs) are used for calibration. This isotope after beta decay disintegrates to its two daughter products, stable barium-137 and the meta-stable, barium-137 m. The latter undergoes gamma emission. When using cesium-137 as a calibration standard to measure the gross beta activity the gamma rate therefore must be converted into the equivalent beta disintegration rate in the calculation. For such conversion, multiply the calibrated gamma emission rate per milliliter or gram by 1.29 to determine the total electrons emitted. Gross beta activity in the sample may also be measured by using strontium-90 (^{90}Sr) as an alternate calibration standard (in equilibrium with its daughter yttrium-90 resulting from beta decay). The calibration standards used for measuring gross alpha activity include many alpha emitting heavy radionuclides, such as, thorium-230, uranium-230, plutonium-239, and americium-241.

For aqueous samples for each 20 cm^2 of counting pan area select an appropriate volume that should contain no more than 200 mg residue for determining beta activity and not more than 100 mg residue for alpha examination. A sample is taken in a borosilicate glass beaker or an evaporating dish and a few drops of methyl orange indicator are added to it. Then, nitric acid, 1 N solution is added dropwise to adjust the pH from 4 to 6. The solution is then evaporated to near dryness on a hot plate or a steam bath. Do not bake the solid. The residue is quantitatively transferred to a tared counting pan with a rubber policeman and small quantities of distilled water (and few drops of acid). Transfer the washings to the counting pan. The sample may be directly added in small increments to a tared counting pan and evaporated slowly below the boiling temperature.

The residue is then dried in an oven at 103°C–105°C, cooled in a desiccator, and weighed. The gross alpha and/or the beta activity in the residue are then counted with a thin-end window counter. Certain radioactive substances that are volatile are susceptible to be lost during the sample evaporation or the drying stage. In addition, the radionuclides of cesium are not recovered if the sample is heated to dull red heat.

Activity of Dissolved and Suspended Matter

The gross alpha and/or beta activity of dissolved matter in the sample is carried out by the above procedure after filtering out the suspended matter or any solid residues through a 0.45 μm membrane filter. For suspended matter, filter the sample through the membrane filter with suction. Select the sample volume appropriately such that for each 10 cm^2 of the membrane filter area the weight of the suspended matter does not exceed 50 mg for the alpha assay and 100 mg for the beta count. The filter is transferred to a tared counting pan and dried in an oven. Saturate the membrane with alcohol and ignite. Cool, weigh, and count the alpha and beta activities on the internal counter. The ignition step may be omitted if the activity is counted with another type of counter. Alternately, determine the total activity and the activity in the dissolved matter. The difference should be equal to the activity of suspended solids in the sample.

The procedural steps outlined above are more or less the same. The important step however is to transfer a thin uniform layer of the sample residue to a tared counting pan in a thin-end window counter. If needed transfer the sample residue, with a few drops of clear acrylic solution and fix it on the tared counting pan of the thin end-window counter as a uniform and thin layer.

Activity of Semisolid Samples

Semisolid nonfatty samples such as sludge and wet soil are well mixed, ground, and powdered with a pestle in a mortar. The total solid content in the sample should be determined prior to measuring

the activity. Transfer the solids, not more than 100 mg for the alpha assay and not more than 200 mg for the beta assay for each 20 cm^2 area of the counting pan. The solid is spread as a thick aqueous cream as a layer of uniform thickness on the tared counting pan, then oven dried, and weighed. Alternatively, the solid sample may be dried first, then mixed with acetone and a few drops of clear acrylic solution and spread on the counting pan, oven dried at 103°C–105°C, and finally weighed before counting. Samples of a vegetation nature may be corrosive to the aluminum counting-pan. For such samples, either use a stainless steel pan or acidify the sample with hydrochloric or nitric acid to a pH between 4 and 6 and then transfer it to the aluminum pan, oven dry at 103°C–105°C, weigh and count the alpha and beta activity. Biological samples such as fatty animal tissues are often difficult to process and therefore subjected to a treatment that is more rigorous. Such biological samples are digested with nitric acid followed by the oxidation with hydrogen peroxide. A measured amount of sample, between 2 and 10 g is taken in a tared silica dish and treated with 25–50 mL of 6 N HNO_3 and 1 mL of 15% H_2O_2. The mixture at first is allowed to stand for several hours, following which it is heated gently and then vigorously until nearly dry. Such acid digestion steps are repeated twice with two more portions, each time using about 15–20 mL of 6 N HNO_3. The heating should be gentle to avoid spattering. The dry mass is then ignited in a muffle furnace at 600°C for 30 min, cooled in a desiccator, mounted on the counter pan, weighed and counted for the alpha and beta activities as described above. The alpha and beta activity are calculated as follows:

$$\text{Alpha activity} = \frac{\text{Net cpm} \times 1000}{2.22e \times \text{mL volume sample counted}}$$

where e is the calibrated overall counting efficiency taking into account for the variation and correction for geometry, backscatter, and sample absorption.

Beta activity, when counted in the presence of the alpha activity may be calculated as follows. When using gas flow proportional counters, the alpha particles are also counted at the beta plateau. The alpha to beta count ratios also vary as the alpha particles are more readily absorbed by the sample than the beta particles with increased thickness. Therefore, correct the amplified alpha count on the beta plateau to determine the alpha amplification factor (M) for use in the equation below for measuring the beta activity. The value of M is determined from the calibration curve plotting calibration standard counts with increasing solid thickness. Heavy radionuclide alpha emitters, such as thorium-230, plutonium-239, or americium-241 are used as standards. The amplification factor, M is the ratio of the net counts per minute (net cpm) on the beta plateau to that in the alpha plateau.

$$\text{Beta activity}, \frac{\text{pCi}}{L} = \frac{B - AM}{2.22 \times D \times V}$$

where

B is the net beta counts at the beta plateau
A is the net alpha counts at the alpha plateau
D is the beta counting efficiency, cpm (or dpm)
V is the sample volume in liter
2.22 is the conversion factor from dpm into pCi, that is, 1 dpm = 2.22 pCi

Coprecipitation Method for Gross Alpha Activity

The coprecipitation method gives increased sensitivity and accurate measurement of gross alpha activity compared to the evaporation method discussed above. While the latter measures both the gross alpha and beta activities in the sample, the coprecipitation method determines only the gross alpha activity. The evaporation method could be susceptible to error if the aqueous sample contains

high dissolved matter in it, usually at levels greater than 500 mg/L. In such a case, the sample size therefore has to be small and consequently the counting time becomes lengthier, which may be assumed a shortcoming of the evaporation method. In the coprecipitation method, the sensitivity of measurement can be improved by using a large volume of sample. Thus, the gross radioactivity of the alpha emitters, such as the heavy elements radium, uranium, and thorium can be determined more accurately in a shorter counting time. The method is based on the principle of separating the alpha emitters from other dissolved substances in the water as insoluble precipitates by using suitable reagents. For example, the soluble salts of heavy radioactive elements can be precipitated out as insoluble barium sulfate with iron hydroxide as the carrier. Other soluble ions in the water may also separate out as mixed precipitate and therefore increase the weight of the precipitate and thus may interfere in the calculation.

Procedure

To 500 mL sample or sample diluted to 500 mL, add five drops of diluted detergent (1:4 dilution with water). The sample is heated under magnetic stirring with gentle addition of 20 mL 2 N H_2SO_4. The solution is boiled for 10 min to expel any CO_2 forming from any carbonate or bicarbonate present in the sample. Boiling also flushes out radon. Reduce the temperature to below boiling and add 1 mL barium carrier solution (prepared by dissolving 4.4 g $BaCl_2 \cdot 2\ H_2O$ in 500 mL distilled water; 1 mL solution = 5 mg Ba^{2+}). Continue stirring for 30 min. Then, add 1 mL bromocresol purple indicator (prepared by dissolving 100 mg in 100 mL distilled water; 0.1% solution), followed by 1 mL iron carrier solution (made by dissolving 17.5 g $Fe(NO_3)_3{\cdot}9H_2O$ in 200 mL water containing 2 mL 16 N HNO_3 and diluted to 500 mL; 1 mL = 5 mg Fe^{3+}), and 5 mL of paper pulp stirred mixture (made by adding 0.5 g paper pulp pellet 500 mL distilled water in a plastic bottle, then five drops of diluted detergent [1:4 dilution], stirred vigorously for 3 h before use). Add 6 N NH_4OH solution dropwise under stirring until the solution becomes alkaline as indicated from a distinct change in color from yellow to purple. The mixture is stirred for 30 min under warming. The precipitate is quantitatively transferred to a glass fiber filter or a membrane-filter (47 mm diameter, 0.45 μm pore size), filtered and washed with 25 mL distilled water. Hold filter for 3 h for any radon progeny to decay. The precipitate is then dried under a heat lamp or in an oven at 105°C. Count the gross alpha activity of the filter with an alpha scintillation counter or a low-background proportional counter. Determine the alpha activity background of the reagent blank precipitate.

$$\text{Gross alpha activity}, \frac{\text{pCi}}{L} = \frac{C_a - C_b}{EV}$$

where

C_a and C_b are the counts per minute, cpm for sample and reagent blank, respectively
E is counter efficiency (cpm/pCi)
V is the volume of sample (L)

Specific Radionuclides

The evaporation and coprecipitation methods mentioned above are mostly used to measure the gross alpha and/or beta activities in samples. The activities of specific radionuclides in the sample can be detected by various methods including the above methods. All these methods mostly differ from each other primarily in the process of their separation and transfer from the sample matrices onto the counter pan. Such separation methods include precipitation or coprecipitation, ion exchange, distillation, and evaporation techniques (ASTM, 1972). The selection of a method is based on the chemical and/or the physical properties of the radioactive element. As far as the instrumentation goes the choice of a counter or a spectrometer to determine radioactivity is based on the radiation

the radionuclide emits, that is, an alpha or a beta particle, or gamma radiation. Use a gamma spectrometer, for example, if the radionuclide emits gamma radiation.

In the ion exchange method, the radioisotope is converted into its ion. For example, the radionuclides of iodine of mass 131 produced in fission reactions may be determined after its separation and concentration from the water on an anion exchange column. In the distillation method, on the other hand, the radionuclide is separated from water and concentrated by distillation. Many radionuclides can be separated from the aqueous sample by more than one method. Most separation methods, however, are based on a combination of some of these techniques. The procedures to determine the activities of some specific radionuclides found in the environment are briefly outlined below. The procedures for collection and preservation of samples are discussed in the literature (U.S. EPA, 1997; USGS, 1997).

Radium

All isotopes of radium are radioactive. It is an alkaline-earth element. The four naturally occurring isotopes of radium are radium-223, radium-224, radium-226, and radium-228 with $t_{1/2}$ of 11.43 days, 3.66 days, 1600 years, and 5.75 years, respectively. Out of these radium-226 and radium-228 are the most important because they are found in many waters and have long half-lives. Radium-228 is a beta emitter, while the other three isotopes are alpha emitters. Radium can be measured by several methods. Some of these methods are outlined below.

Precipitation Method and Alpha Counting

All alpha emitting isotopes of radium can be measured by the precipitation method, followed by alpha counting with a gas flow internal proportional counter or a thin-end window gas flow proportional counter or with an alpha scintillation counter. In this method, radium is coprecipitated out from the water sample into which alkaline citrate is added followed by lead and barium carriers (as $BaCl_2$ and $Pb(NO_3)_2$ solutions). The addition of sulfuric acid to the citrate solution of the sample precipitates out radium, barium, and lead as their insoluble sulfates. The precipitate is washed with nitric acid and dissolved in an alkaline solution of disodium ethylenediaminetetraacetate (solution made alkaline by adding 5 N NH_4OH dropwise before the addition of ethylenediaminetetraacetic acid [EDTA]). Radium–barium sulfate reprecipitates out when the pH of this solution is adjusted to 4.5. This step separates and purifies the radium–barium sulfate, freeing it from lead sulfate and other naturally occurring alpha emitters that remain in the solution. The precipitate is washed, dried at 110°C, and weighed (after being transferred on the tared stainless steel planchet or membrane filter) and the alpha activity is measured with a proportional counter. If using an alpha scintillation counter mount the dry precipitate on a nylon disk and ring, with an alpha phosphor on polyester plastic film and measure the net counts per minute in the total weight of the precipitate. The alpha emitting isotopes have different half-lives and decay rates. To determine the alpha activity, the ingrowth factor (attributed to the difference in half-lives) must be taken into account along with the self-absorption factor and the efficiency factor (of the counter for alpha counting) in the final calculation. The details of determining these factors may be found in the method or in the instrument manuals.

$$\text{Radium}, \frac{\text{pCi}}{L} = \frac{\text{Net cpm}}{2.22^{abcde}}$$

where

a is the ingrowth factor
b is the efficiency factor for alpha counting
c is the self-absorption factor

d is the chemical yield
e is the sample volume (L)

Precipitation and Emanation Method to Measure Radium as Radon-222

This method measures the total radium-226 in the water that includes both the dissolved isotope of this element and that present in the suspended particles. In this method, the radium is measured as its daughter isotope radon-222 resulting from the alpha decay. Radium is separated from water by coprecipitation with barium as sulfate (radium–barium sulfate) using acidified barium chloride solution followed by sulfuric acid. The mixture is stirred vigorously. The precipitate is filtered through a membrane filter and washed with dilute H_2SO_4. The filter is placed in a platinum dish or crucible, and treated with a small quantity of 48% hydrofluoric acid and a few drops of 10% ammonium sulfate solution and evaporated to dryness for the removal of silicates if present and decompose any insoluble radium compounds. The residue is ignited over a small flame to char the filter and burn off the carbon and then treated with 1 mL 85% phosphoric acid and heated over a hot plate first at 200°C and then at 400°C for 30 min. The precipitate fuses into a clear melt. Fuming with phosphoric acid removes the sulfite (SO_3^{2-}). The mixture is then cooled and treated with 6 N HCl, and heated to dissolve radium completely. The solution is diluted with distilled water. The solution is placed in a bubbler, closed, and stored for several days to measure the ingrowth of radon. The bubbler is connected to an evacuation system. The liquid is aerated to purge out the radon gas. Radon may alternatively be purged with helium or nitrogen. It is then dried over a desiccant and collected in a counting chamber. Radon-222 is counted on an alpha scintillation counter. Details of the concentration techniques, scintillation counter assembly, and the radon bubblers are described in the method and the instrument manuals. Calculate radium-226 in the bubbler from the following equation, taking the correction, ingrowth, and decay factors into account:

$$\text{Radium-226, pCi} = \frac{[(R_s - R_b)/R_c]}{(C/AB)}$$

where
R_s is the counting rate of sample per hour (cph), measured in the counting cell
R_b is the background counting rate, cph in the scintillation cell with the counting gas

As measured previously

R_c is the calibration constant for the scintillation cell (observed net counts per hour, with correction for ingrowth and decay, per picocurie of radium in the standard)
A is the factor for decay of radon-222
B is the factor for growth of radon-222
C is the factor for correction for radon-222 activity for the decay during counting
(the factors *A*, *B*, and *C* may be found in the method, instrument manuals, or in the tables in the reference texts for radioactivity)

Sequential Precipitation Method

Soluble radium-228 in water can be determined by beta counting in this method. The method can also be used to analyze both the radium-228 and -226 isotopes in the water. While ^{226}Ra is an alpha emitter, the isotope ^{228}Ra undergoes beta decay converting into actinium-228. In the first step of this method, all radium isotopes are separated out from the water as insoluble barium–lead sulfates with coprecipitation with barium and lead carriers. After this, the precipitate is dissolved in an

EDTA solution for purification by EDTA chelation. If only radium-228 is to be measured, allow 36 h ingrowth of actinium-228. Add yttrium carrier to the solution to precipitate out actinium–yttrium oxalates for beta counting. If radium-226 is to be measured in the presence of radium-228, determine ^{226}Ra sequentially with alpha counting by radon emanation using a scintillation counter assembly. If radium-228 is absent, then the radium-226 fraction may be directly counted for alpha activity. The stepwise procedures in detail including the preparations of reagents and carriers may be found in the *Standard Methods for the Examination of Water and Wastewaters* (APHA, AWWA, and WEF, 2005) and the references under that method (U.S. EPA, 1980).

Measurement of Radium-224 by Gamma Spectroscopy

Radium-224 in water can be measured by this method. Radium is separated from water by coprecipitating out with lead sulfate using a lead carrier. Radium-224 decays to lead-212 and the gamma radiation is measured with a high-resolution intrinsic Ge detector. An aliquot of the sample is treated with anhydrous sodium sulfate and concentrated H_2SO_4, and boiled on a hot plate or a magnetic stirrer under stirring. While under boiling, the lead carrier solution [$(Pb(NO_3)_2$ solution] is added dropwise. This precipitates out $PbSO_4$. The mixture is placed in an ice bath and cooled and washed with a dilute solution of $PbSO_4$ (wash solution). The precipitate is quantitatively transferred and filtered on a preweighed membrane filter (47 mm diameter, 0.45 um porosity). Transfer filter to a planchet. Mount the petri dish containing the coprecipitated sample planchet on the Ge detector to determine the gamma activity. Determine the chemical yield of the $PbSO_4$ precipitate. Count the activity in the prepared calibration standards to determine the efficiency of the detector. Determine the background gamma activity by counting the membrane filter on the planchet without the application of the standard solution. Follow the manufacturer's manual for the sample counting procedure.

Radon

Radon is a radioactive gaseous element in the noble gas group. Radon-222 is the daughter isotope of radium-226 resulting from its alpha decay. It is an alpha emitter with a half-life of 3.82 day. Radon seeps out from the ground resulting from the alpha decay of uranium and other radioactive elements present deep inside the earth. It is susceptible to occur in the air in the basements or the lower levels in houses and in the groundwater wells. Exposures to radon can cause lung cancer. It is one of the leading causes of death from lung cancer in the United States.

Radon-222, the most prevailing and the longest half-life isotope of radon can be measured by the liquid scintillation method (Cothern and Rebers, 1990). It is partitioned selectively from the aqueous samples into a mineral oil scintillation cocktail immiscible in water. Before processing, the sample is dark adapted and equilibrated to room temperature to minimize diffusion. The alpha particles from radon are counted in a liquid scintillation counter at a region of energy spectrum optimal for radon. Follow the instrument's manual for the operational procedure. Use radium-226 aqueous standard solutions for the calibration. Determine the calibration factor, background-counting rate and the decay factor to measure radon-222 concentration in the water.

$$^{222}\mathrm{Rn}, \frac{\mathrm{pCi}}{L} = \frac{(G-B)}{CF \times D \times V}$$

where

G is the gross counting rate of the sample, cpm
B is the background-counting rate
D is the decay factor for ^{222}Rn from the time of the sample collection
V is the sample volume in liter
CF is the calibration factor that is calculated as $(S - B)/CV$

(S is the counting rate, cpm for radium-226 calibration standard; B is the background counting rate, cpm; C is concentration of radium-226 standard in pCi/L; and V is the liter volume of the calibration standard)

Uranium

Uranium is the heaviest naturally occurring element. Its atomic number is 92. All its isotopes are radioactive. The element has three isotopes, uranium-238, uranium-235, and uranium-232. Uranium-238 is the most abundant of these isotopes, and is composed of 99. 275% by mass. The natural abundance of uranium-235 is 0.72% and uranium-232 occurs relatively at trace concentrations (0.005%). Uranium-238 occurs in the earth's crust. Its soluble salts are found in many types of groundwater. The alpha activity of the total uranium in water is measured with a gas-flow proportional counter or alpha scintillation counter.

Determination of Total Alpha Activity

The aqueous sample is first acidified with nitric or hydrochloric acid and then boiled to remove any carbonate or bicarbonate. Uranium is separated from water by the coprecipitation method. Thus, any soluble salts of uranium present in the water are coprecipitated out as insoluble uranium hydroxide along with ferric hydroxide. The procedure involves treating 1 L of the acidified sample with 1 mL of ferric chloride solution (added as $FeCl_3$ carrier, prepared by dissolving 9.6 g $FeCl_3 \cdot 6H_2O$ in 100 mL 0.5 N HCl). The pH of the solution is adjusted to 1. While the sample is being boiled slowly, add a 5 N solution of NH_4OH until the solution becomes turbid due to the formation of insoluble $Fe(OH)_3$. Continue boiling and then add 10 mL more of NH_4OH solution. Allow the mixture to stand for about 30 min to cool. Allow the precipitate to settle. Filter the solution through a 47 mm, 0.45 μm membrane filter. To speed up the filtration, decant the supernate first and then filter the slurry under suction. Wash the precipitate with 1% solution of NH_4OH. Place the filtering apparatus over a 250 mL filtering flask. Add 25 mL of 8 N HCl to the filter to dissolve the precipitate. Wash the filter further with another 25 mL HCl. This dissolves all the ferric-uranium hydroxide. After this, the solution is passed through an anion-exchange column (i.e., Dowex 1 × 4, chloride form, 100–200 mesh or equivalent).

Iron is eluted out first with freshly prepared HCl–HI solution (a mixture of 8 N HCl and 47% HI at a ratio 90:10). This will also elute any plutonium present in the sample. The column is washed with 8 N HCl. Discard the washings. After removing the iron, elute out uranium with the dilute hydrochloric acid (0.1 N HCl). Collect the acid eluates of uranium. Evaporate this eluate to a very small volume, almost to near dryness (do not bake to dryness). The residue is dissolved in 2 mL of 4 N HNO_3. The uranium nitrate solution formed is quantitatively transferred with rinsing to a marked planchet. The solution in the planchet is evaporated to complete dryness first under a heat lamp and then under a flame (to break any trace quantities of HIO_3 formed). The residue is cooled and counted for alpha activity.

To clean up and regenerate the anion exchange column for repeat use wash the column several times with a solution of 1% $NaHSO_3$ in 6 N HCl, and then with 6 N HCl, and finally with distilled water. Do not allow the resin to go dry. To use the column once again pass 8 N HCl several times through the column.

Determination of Isotopic Content of Uranium Alpha Activity

Uranium-232 standard solution (10 dpm/mL in 1 N HNO_3) is used as a tracer to measure the alpha activity of the uranium isotopes in the sample. The sample is acidified with HCl or HNO_3 and the uranium-232 tracer is added into it. Uranium is coprecipitated out from the acidified aqueous sample by the treatment with ferric chloride carrier solution. The details of its separation procedure

including coprecipitation with ferric hydroxide, followed by acid digestion, loading the solution on the anion exchange column or finally eluting uranium from the column are discussed above. Uranium after its separation from the sample is then electrodeposited onto a stainless steel disk to measure its alpha emanation. An alpha spectrometer is used for counting the particles. Such an instrument should have the ability to give a resolution of 50 keV or better and a counting efficiency of greater than 15%. A silicon surface-barrier detector is used to measure the alpha pulse height. The apparatus for electrodeposition consists of a cathode slide that has a 0.05 cm thick mirror finish and an exposed area of 2 cm^2 for the electrodeposition. The anode constitutes a platinum wire of 1 mm diameter with an 8 mm diameter loop at the end. For electrodeposition, use DC power supply of 0–12 V at 0–2 amp.

The total counts for each uranium isotope is determined by summing the counts at the peak at the energy corresponding to the isotope. Complete resolution may be difficult if two isotopes are close in energy. In such a case, subtract the background from each peak. If necessary, perform a blank correction for each peak. Determine the concentration of each uranium isotope from the following equation:

$$U_x, \frac{\text{pCi}}{L} = \frac{C_x A_t}{C_t V}$$

where

U_x is the concentration of the specific isotope of uranium that is being measured
C_x is the net sample counts in the energy region for that uranium isotope
A_t is the activity of the uranium-232 tracer added, expressed in dpm
C_t is the net sample count in the energy region for the uranium-232 tracer
V is the volume of sample, expressed in L

Radioactive Strontium

Strontium has several unstable isotopes in the mass range 79–98. The two most prevalent radioactive isotopes, however, are the ^{89}Sr and ^{90}Sr, both produced in nuclear fission. Strontium-90 is a long-lived high-energy beta emitter with a half-life of 29 years. The half-life of strontium-89 is 51.5 days. Three other radioisotopes of this element, namely, ^{91}Sr, ^{92}Sr, and ^{93}Sr, all beta emitters and short-lived with half-lives of 9.5 h, 2.71 h, and 7.5 min, respectively, however, are not found in the environment. Strontium-90 is of major concern. The target organ in the body for strontium is the bone, where it undergoes ion exchange with calcium and is stored.

The total radioactive strontium in water is measured from the beta activity of its radionuclides after their separation from the water by the precipitation method. Strontium–barium carrier along with sodium hydroxide and sodium carbonate solutions are added at different stages in such procedures to separate the strontium. Such carriers constitute the acidified aqueous solutions of strontium nitrate and barium nitrate. The radionuclides of strontium are first separated from other radioactive elements and also from other inactive sample solids by precipitation as $Sr(NO_3)_2$ upon treatment with fuming nitric acid solution. After this strontium is precipitated out as its insoluble carbonate salt, $SrCO_3$ when treated with sodium carbonate solution.

A large volume of sample, usually 1 L is used to measure any low amount of radioactivity from the strontium isotopes. In the first step of separation, the carriers are added to the aqueous sample. The sample is then heated to boiling. This is followed by addition of 6 N NaOH and 1 M Na_2CO_3 solutions. The mixture is stirred and heated at 90°C for 1 h. The precipitate formed is allowed to settle. Decant and discard the clear supernate. The mixed carbonate precipitate is further centrifuged. Discard the supernate. The carbonates are then converted into their nitrates by successive treatments with concentrated and fuming nitric acid, respectively, in small amounts. The concentrated

nitric acid is added dropwise to the solid mix followed by heating the solution to boiling, and then cooling. After this, fuming nitric acid is added. The mixture is cooled in an ice bath, stirred, and centrifuged. The solid mix separated after centrifuging is boiled in water to dissolve all the strontium (converted into nitrate). Again, centrifuge the solution while hot to separate and discard any insoluble residues of silica, barium sulfate, and other substances that may be present in the sample or may have formed during sample treatment.

The solution is once again treated with sodium hydroxide followed by sodium carbonate solution. The precipitate is centrifuged and washed with distilled water. It is then transferred to a tared paper or glass filter mounted in a two-piece funnel. It is further washed repeatedly with water, 95% ethanol, and dry acetone and then dried in an oven at 110°C for about 30 min. After cooling and weighing the precipitate is mounted on a nylon disk, covered with a polyester plastic film and counted for beta activity. The total Sr activity is calculated as follows:

$$\text{Total Sr activity, } \frac{\text{pCi}}{L} = \frac{b}{2.22adf}$$

where

b is the beta activity, measured as net cpm and is determined from the equation $(i/t) - k$
(where i is the total counts accumulated, t is the time of counting in minutes, and k is the background, cpm)
a is the beta counter efficiency
f is the sample volume in liter
d is the ratio of the weight in mg of the final $SrCO_3$ precipitate to the amount in mg of $SrCO_3$ in 2 mL carrier (for correction for carrier recovery).

The above procedure, however, would not apply if only strontium-90 and not the total strontium activity is to be measured in the sample. This is because both the radionuclides of Sr, namely, the ^{90}Sr and ^{89}Sr cannot be separated by the precipitation method or by any other chemical process because their chemical properties are similar. The amount of ^{90}Sr in the sample is determined by separating its daughter isotope yttrium-90 and then measuring the activity of the latter. It may be noted that the activity of ^{90}Sr is exactly equal to the activity of ^{90}Y after the equilibrium is reached. Yttrium-90 is separated by acidifying the sample with concentrated nitric acid and then extracting the solution with tributyl phosphate. Yttrium-90 is then back extracted into dilute nitric acid and the solution is evaporated to dryness for beta counting. An alternative method consists of adding an yttrium carrier and ammonium hydroxide to the sample. Yttrium hydroxide, $Y(OH)_3$ precipitate is centrifuged and separated, washed and converted into yttrium nitrate by treatment with nitric acid. The water-soluble yttrium nitrate is dissolved in water and treated with oxalic acid to precipitate out yttrium oxalate. The precipitate is washed successively with water, 95% ethanol, and diethyl ether and air-dried. It is then weighed, mounted on a nylon disk, covered with polyester plastic film, and counted in an internal proportional or end-window counter to measure the beta activity of ^{90}Sr. The activity is measured as follows:

$$^{90}\text{S, } \frac{\text{pCi}}{L} = \frac{\text{Net cpm}}{2.22^{abcdfg}}$$

where

a is the counting efficiency for ^{90}Y
b is the chemical yield of precipitating ^{90}Y
c is the ingrowth correction factor
d is the chemical yield of strontium

f is the sample volume (L)
g is the decay factor for ^{90}Y, which is determined from $e^{-(0.693/T½)t}$
(the half-life, $T_{½}$ for ^{90}Y is 64.2 h and t is the time in hours between the separation and counting)

Tritium

Tritium is a radioactive isotope of hydrogen. Its mass number is 3. It is produced naturally by the interaction of cosmic rays with hydrogen. It is also detected in the residual fallout from nuclear tests. It is also produced in nuclear reactors (light-water nuclear reactors) to generate electricity. Tritium decays by beta emission to helium-3. Its half-life is 12.26 years. The maximum beta energy of tritium is 0.018 MeV.

Tritium is determined by liquid scintillation spectrometry. Liquid scintillation materials are available commercially or may be prepared. The scintillation solution can be made from dissolving 4 g of 2,5-diphenyloxazole, 0.05 g 1,4-di-2-(5-phenyloxazolyl)benzene, and 120 g solid naphthalene in 1 L spectroscopic grade 1,4-dioxane. The solution should be stored in dark bottles and should be stable for 2 months. In this method, the aqueous sample is treated with alkaline potassium permanganate solution and distilled to almost to near dryness. Such distillation removes most quenching materials as well as some other radionuclides, especially that of iodine and carbon. The distillate is mixed with scintillation solution and the beta activity is counted on a liquid scintillation spectrometer.

To a 100 mL sample placed in a 250 mL distillation flask, add three pellets of NaOH and 0.1 g $KMnO_4$. Distill the solution at 100°C. Discard the first 10 mL distillate, then collect the next 50 mL. Place 4 mL of distillate in a tightly capped vial, add 16 mL scintillation solution, and thoroughly mix the solution. Treat low-background water and the tritium standard solution in the same manner subjecting to distillation and adding the scintillation solution. Place the sample, background, and the standard solutions in dark for 3 h and count for beta activities. Samples containing more than 200 pCi/mL should be counted for 50 min, however, if the beta activity is less, then count for 100 min. Calculate the beta activity of tritium as follows:

$$^{3}\mathrm{H}, \frac{\mathrm{pCi}}{\mathrm{mL}} \quad \left(\text{or} \frac{\mathrm{nCi}}{L}\right) = \frac{(C - D)}{E \times 4 \times 2.22}$$

where
C is the gross counting rate for sample (cpm)
E is the counting efficiency, measured as $(S - B)/D$
(where S is the gross counting rate for the standard solution, cpm; B is the background counting rate (cpm); and D is the tritium activity in the standard solution corrected for the decay for time of counting)

Radioactive Iodine

Iodine forms several radioisotopes, in the mass range 129–135. Among these, iodine-131 has the highest specific activity, 1.24×10^5 Ci/g with a half-life of 8 days. In comparison, iodine-129 has the longest half-life, 1.6×10^7 years. Its specific activity, however, is relatively low, 1.73×10^{-4} Ci/g. The radioisotopes of this element are produced as fission products in nuclear tests or released during use and processing of fuels in nuclear reactors. Iodine-131 is found in the environment. Exposure can cause thyroid cancer. Iodine-131 in aqueous samples can be measured by three different methods; one is precipitation, while the other two are ion-exchange and distillation methods. These methods are discussed above under other radioisotopes. The detection limit of measuring 1 pCi iodine-131 per liter sample can be achieved by all these methods.

Precipitation Method

The precipitation procedure is relatively simple and the time of analysis is lesser than the other two methods. In this method, 2 L of sample is acidified with nitric acid. The acidified sample is then treated with 1 mL iodate carrier (prepared by dissolving 1.685 g KIO_3 in 100 mL water, storing the solution in dark, 1 mL = 10 mg L) followed by 4 mL of freshly prepared 1 M Na_2SO_3. The latter is added to reduce the iodate to iodide. The mixture is stirred for 30 min. This is followed by addition of 20 mL of 0.1 M $AgNO_3$ to precipitate out all the iodide together with ^{131}I from the solution. Stir the mixture for 1 h during this precipitation process. Allow the precipitate to settle for an hour. Decant the supernatant and discard. Filter the precipitate on a glass fiber filter. Discard the filtrate.

Place the filter in a centrifuge tube. Add a small quantity of distilled water to the precipitate to prepare slurry. Add about 1 g zinc powder and 2 mL 2 N H_2SO_4 to this slurry and stir for 30 min to convert the insoluble silver iodide into the soluble zinc iodide. The mixture is filtered through a fine-fritted glass funnel under vacuum. Wash the residue and filter, and collect the filtrate and washings that now contain iodine-131. Discard the residue. The filtrate is acidified with 2 mL of 6 N HCl and heated for 10 min at 80°C in a water bath. Add 1 mL of 0.2 M $PdCl_2$ solution to this and heat for 5 min. This converts ZnI_2 to the insoluble PdI_2. The PdI_2 precipitate is centrifuged and the supernatant discarded. The precipitate is dissolved in 6 N NH_4OH and the solution heated for a few minutes in a boiling water bath. The PdI_2 is reprecipitated after neutralizing the solution with 6 N HCl and adding 1 mL of 0.2 M $PdCl_2$ followed by heating. This step is carried out for purification and removal of all interference. The precipitate now contains all the radionuclide, ^{131}I from the sample. It is finally transferred to a tared filter, washed with distilled water and then 95% ethanol, dried in a vacuum oven at 60°C, weighed, mounted, and counted for beta activity with a low-background beta counter or a gamma spectrometer. The concentration of iodine-131 is calculated as follows:

$$\text{Iodine-131}, \frac{\text{pCi}}{L} = \frac{C}{2.22EVRA}$$

where

C is the net count rate (cpm)
E is the counting efficiency of ^{131}I as function of mass of precipitate, PdI_2
R is the fractional chemical yield, (PdI_2 recovered × 0.0704)/iodine carrier added
A is the decay factor for ^{131}I for the time interval between sample collection and measurement

Ion-Exchange Method

In this procedure, a known quantity of inactive iodine is added to the sample as a carrier. Potassium iodide is mostly used as a carrier as it is the inactive form of iodine. All iodine in the sample is first reduced to the iodide ion. Hydroxylamine hydrochloride and sodium bisulfite are used as the reducing agents. Iodine as iodide is then concentrated by the absorption on an anion-exchange column, followed by elution with sodium hypochlorite solution and oxidation to iodate by heating with NaOCl–HNO_3. The iodate is reduced to I_2 by the hydroxylamine bisulfite. I_2 is extracted into carbon tetrachloride and back-extracted as iodide into the water. After this series of concentration and purification of iodine in the sample, it is finally precipitated as palladium iodide by treatment with $PdCl_2$ solution. The procedures for these steps are given below.

To a 1 L sample in a beaker add 2 mL of iodine carrier solution and then 5 mL of 5% NaOCl solution. Heat the mixture for a few minutes to complete the oxidation of the iodine into iodide. After this, add 5 mL concentrated nitric acid slowly followed by 25 mL of 1 M solution of NH_2OH. HCl. Stir the mixture and then add 10 mL of 1 M $NaHSO_3$. Adjust the pH to 6.5. Stir the mixture thoroughly and filter the solution through a glass fiber filter. Collect the filtrate and discard the residue.

Place the anion-exchange resin (20 g) in a column and wash with some water. Pass the sample through the anion-exchange column at a flow rate of 20 mL/min. Discard the effluent after passage through the column. Wash the column first with 200 mL of distilled water followed by 100 mL of 2 M NaCl solution at a flow rate of 4 mL/min. Discard the washings. Load the column with 50 mL of 5% NaOCl solution in increments of 10 mL. Pass this solution through the column at a flow rate of 2 mL/min. Collect the eluant in a beaker. Add slowly about 10 mL of conc. HNO_3 adjusting the normality of the acid between 2 and 3. Transfer this solution to a separatory funnel.

To the above solution in the separatory funnel, add 50 mL of carbon tetrachloride and 10 mL of 1 M $NH_2OH{\cdot}HCl$. Shake the mixture well to extract all I_2 from the aqueous to CCl_4 phase. Allow the phase to separate. Transfer the bottom CCl_4 into another separatory funnel. Extract the top aqueous phase once again with 25 mL of CCl_4 and 5 mL of $NH_2OH{\cdot}HCl$ solution, and shake vigorously for 1 or 2 min for the second extraction. Combine both the CCl_4 extracts and discard the wash solution. Wash the combined organic extract with 20 mL of $NH_2OH{\cdot}HCl$ wash solution.

The organic phase now contains all the iodine from the sample. Add 25 mL of distilled water followed by 10 drops of 1 M $NaHSO_3$ to it and shake vigorously for 2 min. Allow the phases to separate. Discard the organic phase. Transfer the aqueous phase into a beaker. To this, add 10 mL of 3 M HCl, and boil over a hot plate under stirring until it starts turning yellow or to a final volume of 10–15 mL. To this, add about 1 mL of $PdCl_2$ and 15 mL of 1 N HCl and stir the solution. Place the beaker in a stainless steel tray and store at 4°C. Filter the precipitate through a tared filter mounted on a filter holder. The precipitate is washed with 1 N HCl followed by absolute alcohol and dried in a vacuum oven at 60°C for 1 h. It is then cooled in a desiccator, weighed, covered with polyester plastic film, sealed with polyester tape, and counted. The concentration of iodine-131 in the sample is calculated as shown above under the precipitation method.

Distillation Method

In this method, the iodide carrier is added to the acidified sample. The mixture is distilled into caustic soda solution followed by a series of purification steps similar to that in the other procedures. The distillate collected from the distillation of the sample with iodide carrier is acidified and shaken with carbon tetrachloride. Iodine is extracted into carbon tetrachloride. It is then converted into iodide by oxidation and reduction with $NaNO_2$ and $NaHSO_3$, respectively. Treatment with $PdCl_2$ solution precipitates all iodide as PdI_2 for counting. The major steps of this method are outlined below.

Place 2 L of sample in a 3 L round-bottomed flask. Add 15 mL of 50% tartaric acid solution (50 g in 100 mL distilled water) and 1 mL of iodide carrier (made from mixing 2.1616 g KI and two drops of $NaHSO_3$ and 100 mL distilled water; 1 mL of this solution contains 20 mg iodine). The mixture is shaken well. To this mixture, add cautiously 25 mL of cold nitric acid. The flask is connected to a distillation set up. The mixture is distilled while adjusting the flow rate to about two bubbles per second. Distill for about 15 min. Collect the distillate over 15 mL of 0.5 N NaOH solution. Cool and transfer the NaOH solution to a 50 mL separatory funnel. Add 1 mL of 12 N H_2SO_4 to this and adjust the pH of this solution to slightly acidic. To this, add 1 mL of 1 M $NaNO_2$ followed by 10 mL of carbon tetrachloride. Shake the mixture vigorously for 1–2 min. Allow both the immiscible layers to separate.

Transfer the bottom organic layer into a clean separatory funnel containing 2 mL of 1 M Na_2SO_3. Carry out a second extraction of the aqueous layer above with 5 mL of carbon tetrachloride and 1 mL of 1 M $NaNO_2$ repeating the above steps. Combine both the organic fractions in the second separatory funnel. Discard the aqueous layer. This carbon tetrachloride solution should now contain all the iodide in the sample and the carrier as iodine. On top of this organic layer is a small aqueous layer containing the reducing agent Na_2SO_3. Shake the separatory funnel vigorously until the color of the iodine in the CCl_4 solution decolorizes. All of the iodine present in CCl_4 is reduced back to the iodide by the reaction with Na_2SO_3. Iodide is water-soluble and therefore

partitions into the aqueous phase. Allow both the phases to separate. Transfer the aqueous layer into a centrifuge tube. Perform a repeat extraction of CCl_4 phase with another 1 mL of distilled water as above to ensure complete removal of any trace iodide that may still be present in the CCl_4. Transfer the second aqueous layer and combine with the first aqueous fraction in the centrifuge tube. Discard the CCl_4 phase.

Acidify the combined aqueous fraction with 2 mL of 6 N HCl. Heat the solution for 10 min in a water bath at 80°C. Add 1 mL of $PdCl_2$ solution (made by mixing 3.3 g of $PdCl_2$ in 100 mL of 6 N HCl; 1 mL = 20 mg Pd) dropwise under stirring. Heat gently for 15 min. Cool the mixture. The insoluble PdI_2 precipitates out. Transfer the precipitate to a tared filter mounted in a two-piece funnel. Allow the precipitate to settle by gravity for uniform deposition, and then apply suction. Wash the precipitate successively with 10 mL each of 6 N HCl, distilled water, and 95% ethanol, respectively. Dry for 1 h at 600°C in a vacuum oven. Cool in a desiccator. Weigh the residue and mount for beta counting. The concentration of the radionuclide ^{131}I is calculated as shown above under the section Precipitation Method.

Radioactive Cesium

Two isotopes of cesium are radioactive, ^{134}Cs and ^{137}Cs with half-lives 2 and 30 years, respectively. Both the isotopes are beta and gamma emitters. These radionuclides are produced in nuclear fission. Chronic exposure to these isotopes through ingestion results in the cesium depositing over the soft tissues in the body. Residence time in these tissues, however, is relatively shorter than many other metals.

Radioactive cesium can be measured with either a gamma spectrometer or a low-background beta counter. The activity of high cesium can be directly measured by gamma counting using a large volume of sample, usually 4 L. Alternatively, the sample is evaporated to near dryness for counting. If the activity of cesium is low the preferred procedure, however, should be the precipitation method where the cesium is separated from the interfering substances first by treatment with ammonium phosphomolybdate reagent and then finally separated via a series of steps and precipitated as Cs_2PtCl_6.

To 1 L of sample, add 1 mL of cesium carrier (1.267 g CsCl/100 mL water). Acidify the solution with concentrated HCl (adding about 8.6 mL HCl to make the solution to 0.1 N HCl). Slowly add 1 g ammonium phosphomolybdate $[(NH_4)_3PMo_{12}O_{40}]$. Stir the solution for 30 min with a magnetic stirrer. Allow the precipitate that now contains cesium to stand for 4 h. Decant out and discard the supernatant. Transfer the precipitate quantitatively using 1 N HCl to a centrifuge tube. Centrifuge and discard the supernatant. Wash the precipitate I N HCl and discard the washing. Dissolve the precipitate in about 5 mL of 6 N NaOH, adding the alkali dropwise. Boil off the ammonia by heating the solution over a flame for several minutes. Dilute the solution to 20 mL with distilled water. To remove molybdenum, add 10 mL of 3 M $CaCl_2$ to the above solution and adjust the pH to 7 with 6 N HCl to precipitate the calcium molybdate ($CaMoO_4$). Stir the mixture and centrifuge. Collect the supernatant. Wash the precipitate with distilled water, filter the mixture, and combine the washings to the supernatant that now should contain all of the cesium. Discard the precipitate.

Add 2 mL of 0.1 M H_2PtCl_6 (chloroplatinic acid) and 5 mL of ethanol to the filtrate. Cool and stir the mixture in an ice bath for about 10 min. Wash the precipitate with distilled water, 0.1 N HCl and ethanol successively. Dry the residue at 1100°C for 30 min. Cool, weigh, and mount on a nylon disk and risk covered with polyester plastic. Perform a gamma scan or a beta count with a gamma spectrometer or a low-background beta counter to measure the total radioisotopes of cesium. Calculate the concentration of radio-cesium as follows:

$$\text{Cs}, \frac{\text{pCi}}{L} = \frac{C}{2.22EVR}$$

where

C is the net count rate per minute, cpm
E is the efficiency of the counter
V is the sample volume (L)
R is the fractional chemical yield (in the purification and precipitation process)

Preparation of Ammonium Phosphomolybdate, $(NH_4)_3PMo_{12}O_{40}$ Reagent Solution

To 250 mL of distilled water, add 140 mL of concentrated NH_4OH. To this solution, add 100 g of molybdic acid (85% MoO_3). Stir the mixture, filter and add 60 mL of conc. HNO_3. This is ammonium molybdate, $(NH_4)_6Mo_7O_{24}$ solution. Prepare a dilute solution of nitric acid by adding slowly 400 mL of conc. HNO_3 to 960 mL water. Allow both the solutions to cool to room temperature. Mix both the ammonium molybdate and nitric acid solutions with constant stirring. Allow the mixture to stand for 24 h. Filter and discard the residue. Heat the filtrate to 50°C (not above 55°C). To this filtrate, add sodium-dihydrogen phosphate solution (25 g in 100 mL distilled water). Stir the mixture occasionally. Filter the ammonium phosphomolybdate precipitate. Wash the precipitate with 1% potassium nitrate (KNO_3) solution and distilled water. Dry the precipitate at 100°C for 3–4 h. Transfer the solid into a bottle and store in a desiccator.

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55 Semivolatile Organic Compounds

The term "semivolatile compounds" crudely refers to organic compounds that are not volatile and have higher boiling points, usually greater than that of water, and have correspondingly low vapor pressure. Thus, a large number of substances of wide chemical properties and structural features should fall under this broad category. Several compounds, however, may overlap under both terms, volatile and semivolatile. For analyzing the aqueous samples, the substances should be practically insoluble or should have very low solubility in water for their extraction from the aqueous phase into an immiscible organic solvent for their trace analyses. Such LLE, furthermore, is based on partitioning of trace organics from an aqueous to an immiscible organic phase by pH adjustments. Thus, when an aqueous sample is acidified to a pH below 2, the compounds that are acidic in nature, such as carboxylic acids and chlorophenoxy acids and those that are very weakly acidic, such as phenols, partition from the aqueous phase into a neutral or basic organic solvent that is immiscible in water and exhibit greater solubility in it. In the same way, basic compounds such as amines, imines, amides, imides, and several weak bases can be transferred from aqueous samples into a suitable immiscible organic solvent by adjusting the pH of the waters to greater than 10. Neutral compounds such as polynuclear aromatics or the PCBs can be effectively transferred from the aqueous phase under these conditions as well. However, this depends on their greater solubility in the solvent used. In nonaqueous matrices, such as soil, sediments and hazardous waste such acid–base partitioning is not required. Several extraction procedures are known that may be applied for semivolatile or nonvolatile type substances from aqueous and nonaqueous matrices that include separatory funnel LLE, continuous LLE, Soxhlet extraction, ultrasonic extraction and waste dilution, depending on the sample matrix and the nature and type of compounds. Such extraction procedures are presented in detail in Chapter 5.

The semivolatile compounds in environmental matrices may be analyzed by various methods, some of which are briefly discussed below. Table 55.1 lists the U.S. EPA methods and the procedure described in the Standard Methods for the Examination of Water and Wastewater. All these methods follow more or less the same procedures. The detection limits, however, may differ for regulatory purposes. For example, while the MDL for an acid extractable compound, pentachlorophenol by the EPA Method 525 for potable water is 1.0 μg/L, its MDL in Method 625 for wastewater is whereas the estimated quantitation limit (which is not the same as the MDL) for this compound in the Method 8270 for ground water is 50 μg/L. Such variation may be attributed along with other factors to the extraction procedure and the magnitude of the sample concentration. All these methods are based on extracting the organic analytes by an appropriate technique, followed by concentration, cleanup of the sample extracts for the removal of the interfering substances, and then separation of the compounds in the sample extract on a capillary GC column and subsequently identifying and quantifying the compounds by mass spectrometry. In addition, all these analytical methods to identify and quantify the semivolatile organic compounds in the environmental matrices inherently are based on GC/MS analysis, although their extraction methods may differ. Cleanup steps for the sample extracts may be avoided for clean samples or if no interfering substances are expected to be present. These methods are briefly highlighted below. Methods 8270 and 526 (U.S. EPA Solid Wastes; U.S. EPA Analytical Method 526), however, are described in detail than the other procedures.

U.S. EPA Method 8270. Table 55.2 presents the names of the 238 compounds that are listed under U.S. EPA's Solid Wastes Method 8270D. The compounds in Table 55.2 are listed in the order

TABLE 55.1
Methods of Analysis of Semivolatile Organics

Method Number	Matrices	Extraction Technique
U.S. EPA Method 525	Potable waters	LLE
U.S. EPA Method 625	Wastewaters	LLE
U.S. EPA Method 8270D	Soils, solid wastes, and waters	LLE, ultrasonic, Soxhlet, and waste dilution
U.S. EPA Method 8275A	Soils, sludges, and solid wastes	Thermal extraction (for PAHs and PCBs)
Standard Methods 6410	All aqueous samples	LLE

Note: LLE, liquid–liquid extraction; PAHs, polynuclear aromatic hydrocarbons; PCBs, polychlorinated biphenyls.

of their increasing retention times as they elute out from the GC capillary column. The retention times given in Table 55.2 are for the GC/MS operating conditions given below as specified in this method and may vary under other conditions such as the type and the dimensions (column length, its internal diameter, and film thickness) and the temperature programming used in the analysis. Also presented in Table 55.2 are the CAS Registry numbers of the compounds and their primary and secondary characteristic mass ions for identification. Quantitation compounds of similar types not listed under this method can also be analyzed by this procedure. It may be noted here that some compounds coelute at the same retention times on this column under the analytical conditions. In addition, some compounds that are structurally similar and produce the same mass spectra may also show peaks at retention times overlapping each other. In such cases, confirming the presence of such compounds solely from their mass spectra or from their retention times may be inaccurate and therefore require more scrutiny and use of an alternative column or conditions or even other techniques.

Method 8270 is used to measure the concentration of the semivolatile organic compounds in many types of aqueous and nonaqueous matrices. The compounds are extracted into an appropriate organic solvent and concentrated down to a small volume that is accurately measured. The sample extract is injected into a GC equipped with a narrow-bore fused-silica capillary column to separate the compounds for their detection by a mass spectrometer interfaced to the GC. The mass spectra of the target compounds are compared with that of authentic standards. The response of major quantitation ions of the compounds detected in the sample extract are compared relative to an internal standard using an appropriate calibration curve for their quantitation. Some of the internal standards used in this method are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. The surrogates for this method include 2-fluorobiphenyl, 2-fluorophenol, nitrobenzene-d_5, phenol-d_6, terphenyl-d_{14}, and 2,4,6-tribromophenol. Quantification of multicomponent analytes, such as aroclors, toxaphene, and chlordane by this method may not be accurate.

The GC column used for this method is a silicone-coated fused silica capillary column of 30 m length and 0.25 m internal diameter (or 0.32 m ID) with 1 um film thickness, such as, DB-5 (J & W Scientific, Folsom, California) or equivalent. The GC is interfaced to a MS. The GC to MS interface must give acceptable calibration points at 50 ng per injection for each compound of interest and meet acceptable tuning performance criteria. For a narrow-bore column, the interface is usually capillary-directed into the mass spectrometer source. The mass spectrometer is a quadrupole mass selective detector capable of scanning mass from 35 to 500 amu every 1 s or less using 70 V nominal electron energy in the electron-impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for DFTPP when 1 μL of this tuning standard (50 ng) is injected through the GC to meet the ion abundance criteria as specified in this method and given in Table 55.3. An ion trap detector may be alternatively used if it is capable of axial modulation to

TABLE 55.2
Semivolatile Organic Compounds and Their Retention Times and Characteristic Mass Ions (U.S. EPA Method 8270)

Compounds/CAS Number	RT (min)	Primary Mass Ion	Secondary Mass Ions
2-Picoline [109-06-8]	3.75	93	66, 92
Aniline [62-53-3]	5.68	93	66, 65
Phenol [108-95-2]	5.77	93	65, 66
Bis(2-chloroethyl)ether [111-44-4]	5.49	93	63, 95
2-Chlorophenol [95-57-8]	5.97	128	64, 130
1,3-Dichlorobenzene [541-73-1]	6.27	146	148, 111
1,4-Dichlorobenzene-d_4 (IS)	6.35	152	150, 111
1,4-Dichlorobenzene [106-46-7]	6.40	146	148, 111
Benzyl alcohol [100-51-6]	6.78	108	79, 77
1,2-Dichlorobenzene [95-50-1]	6.85	146	148, 111
N-Nitrosomethylethylamine [10595-95-6]	6.97	88	42, 43, 56
Bis(2-chloroisopropyl)ether [39638-32-9]	7.22	42	77, 121
Ethyl carbamate [51-79-6]	7.27	62	44, 45, 74
Benzenethiol [108-98-5] (thiophenol)	7.42	110	66, 109, 84
Methyl methanesulfonate [66-27-3]	7.48	80	79, 65, 95
N-Nitrosodi-*n*-propylamine [621-64-7]	7.55	70	42, 101, 130
Hexachloroethane [67-72-1]	7.65	117	201, 199
Maleic anhydride [108-31-6]	7.65	54	98, 53, 44
Nitrobenzene [98-95-3]	7.87	77	123, 65
Isophorone [78-59-1]	8.53	82	95, 138
N-Nitrosodiethylamine [55-18-5]	8.70	102	42, 51, 44, 56
2-Nitrophenol [88-75-5]	8.75	139	109, 65
2,4-Dimethylphenol [105-67-9]	9.03	122	107, 121
p-Benzoquinone [106-51-5]	9.13	108	54, 82, 80
Bis(2-chloroethoxy)methane [111-91-1]	9.23	93	95, 123
Benzoic acid [65-85-0]	9.38	122	105, 77
2,4-Dichlorophenol [120-83-2]	9.48	162	164, 98
Trimethyl phosphate [512-56-1]	9.54	110	79, 95, 109, 140
Ethyl methanesulfonate [62-50-0]	9.62	79	109, 97, 45, 65
1,2,4-Trichlorobenzene [120-82-1]	9.67	180	182, 145
Naphthalene-d8 (IS)	9.75	136	68
Naphthalene [91-20-3]	9.82	128	129, 127
Hexachlorobutadiene [87-68-3]	10.33	225	213, 227
Tetraethyl pyrophosphate [107-49-3]	11.07	99	155, 127, 81, 109
Diethyl sulfate [64-67-5]	11.37	139	45, 59, 99, 111, 125
4-Chloro-3-methylphenol [59-50-7]	11.68	107	144, 142
2-Methylnaphthalene [91-57-6]	11.87	142	141
2-Methylphenol [95-48-7]	12.40	107	108, 77, 79, 90
Hexachloropropene [1888-71-7]	12.45	213	211, 215, 117, 106, 141
Hexachlorocyclopentadiene [77-47-4]	12.60	237	235, 272
N-Nitrosopyrrrolidine [930-55-2]	12.65	100	41, 42, 68, 69
Acetophenone [98-86-2]	12.67	105	71, 51, 120
4-Methylphenol [106-44-5]	12.82	107	108, 77, 79, 90
2,4,6-Trichlorophenol [88-06-2]	12.85	196	198, 200
o-Toluidine [95-53-4]	12.87	106	107, 75, 51, 79

(*Continued*)

TABLE 55.2 (*Continued*)
Semivolatile Organic Compounds and Their Retention Times and Characteristic Mass Ions (U.S. EPA Method 8270)

Compounds/CAS Number	RT (min)	Primary Mass Ion	Secondary Mass Ions
3-Methylphenol [108-39-4]	12.93	107	108, 77,79, 90
2-Chloronaphthalene [91-58-7]	13.30	162	127, 164
N-Nitrosopiperidine [100-75-4]	13.55	111	42, 55, 56, 41
1,4-Phenylenediamine [106-50-3]	13.62	108	80, 53, 54, 52
1-Chloronaphthalene [90-13-1]	13.65	162	127, 164
2-Nitroaniline [88-74-4]	13.75	65	92, 138
5-Chloro-2-methylaniline [95-79-4]	14.28	106	141, 140, 77, 89
Dimethyl phthalate [131-11-3]	14.42	163	194, 164
Acenaphthylene [208-96-8]	14.57	152	151, 153
2,6-Dinitrotoluene [606-20-2]	14.62	165	63, 89
Phthalic anhydride [85-44-9]	14.62	104	76, 50, 148
o-Anisidine [90-04-0]	15.00	108	80, 123, 52
3-Nitroaniline [99-09-2]	15.02	138	108, 92
Acenaphthene-d_{10} (IS)	15.05	166	162, 160
Acenaphthene [83-32-9]	15.13	154	153, 152
2,4-Dinitrophenol [51-28-5]	15.35	184	63, 154
2,6-Dinitrophenol	15.47	162	164, 126, 97, 63
4-Chloroaniline [106-47-8]	15.50	127	129, 65, 92
Isosafrole [120-58-1]	15.60	162	131, 104, 77, 51
Dibenzofuran [132-64-9]	15.63	168	139
2,4-Diaminotoluene [95-80-7]	15.78	121	122, 94, 77, 104
2,4-Dinitrotoluene [121-14-2]	15.80	165	63, 89
4-Nitrophenol [100-02-7]	15.80	139	109, 65
2-Naphthylamine [91-59-8]	15.00	143	115, 116
1,4-Naphthoquinone [130-15-4]	16.23	158	103, 102, 76, 50, 130
p-Cresidine [120-71-8]	16.45	122	94, 137, 77, 93
Dichlorovos [62-73-7]	16.48	109	185, 79, 145
Diethyl phthalate [84-66-2]	16.70	149	185, 150
2,4,5-Trimethylaniline [137-17-7]	16.70	120	135, 134, 91, 77
2,4,5-Trimethylaniline [137-17-7]	16.70	120	135, 134, 91, 77
N-Nitrosodi-*n*-butylamine [924-16-3]	16.73	84	57, 41, 116, 158
4-Chlorophenyl phenyl ether [7005-72-3]	16.78	204	206, 144
Hydroquinone [123-31-9]	16.93	110	81, 53, 55
4,6-Dinitro-2-methylphenol [534-52-1]	17.05	198	51, 105
Resorcinol [108-46-3]	17.13	110	81, 82, 53, 69
N-Nitrosodiphenylamine [86-30-6]	17.17	169	168, 167
Safrole [94-59-7]	17.23	162	104, 77, 103, 135
Hexamethyl phosphoramide [680-31-9]	17.33	135	44, 179, 92, 42
3-(Chloromethyl)pyridine hydrochloride [6959-48-4]	17.50	92	127, 129, 65, 39
Diphenylamine [122-39-4]	17.54	169	168, 167
1,2,4,5-Tetrachlorobenzene [95-94-3]	17.97	216	214, 179, 108, 143, 218
1-Naphthylamine [134-32-7]	18.20	143	115, 89, 63
1-Acetyl-2-thiourea [591-08-2]	18.22	118	43, 42, 76
4-Bromophenyl phenyl ether [101-55-3]	18.27	248	250, 141
Toluene diisocyanate [584-84-9]	18.42	174	145, 173, 146, 132, 91

(*Continued*)

TABLE 55.2 (*Continued*)
Semivolatile Organic Compounds and Their Retention Times and Characteristic Mass Ions (U.S. EPA Method 8270)

Compounds/CAS Number	RT (min)	Primary Mass Ion	Secondary Mass Ions
2,4,5-Trichlorophenol [95-95-4]	18.47	196	198, 97, 132, 99
Hexachlorobenzene [118-74-1]	19.65	284	142, 249
Nicotine [54-11-5]	18.70	84	133, 161, 162
Pentachlorophenol [87-86-5]	19.25	266	264, 268
5-Nitro-*o*-toluidine [99-55-8]	19.27	152	77, 79, 106, 94
Thiozanine [297-97-2]	19.35	107	96, 97, 143, 79, 68
4-Nitroaniline [100-01-6]	19.37	138	65, 108, 92, 80, 39
Phenanthrene-d_{10} (IS)	19.55	188	94, 80
Phenanthrene [85-01-8]	19.62	178	179, 176
Anthracene [120-12-7]	19.77	178	176, 179
1,4-Dinitrobenzene [100-25-4]	19.83	168	75, 50, 76, 92, 122
Mevinphos [7786-34-7]	19.90	127	192, 109, 67,164
Naled [300-76-5]	20.03	109	145, 147, 301, 79, 189
1,3-Dinitrobenzene [99-65-0]	20.18	168	76, 50, 75, 93, 122
Diallate (*cis*- or *trans*-) [2303-16-4]	20.57	86	234, 43, 70
1,2-Dinitrobenzene [528-29-0]	20.58	168	50, 63, 74
Diallate (*trans*- or *cis*-) [2303-16-4]	20.78	86	234, 43, 70
Pentachlorobenzene [608-93-5]	21.35	250	252, 108, 248, 215, 254
5-Nitro-*o*-anisidine [99-59-2]	21.50	168	79, 52, 138, 153, 77
Pentachloronitrobenzene [82-68-8]	21.72	237	142, 214, 249, 295, 265
4-Nitroquinoline-1-oxide [56-57-5]	21.73	174	101, 128, 75, 116
Di-*n*-butyl phthalate [84-74-2]	21.78	149	150, 104
2,3,4,6-Tetrachlorophenol [58-90-2]	21.88	232	131, 230, 166, 234, 168
Dihydrosaffrole	22.42	135	64, 77
Demeton-O [298-03-3]	22.72	88	89, 60, 61, 115, 171
Fluoranthene [206-44-0]	23.38	202	101, 203
1,3,5-Trinitrobenzene [99-35-4]	23.68	75	74, 213, 120, 91, 63
Dicrotophos [141-66-2]	23.82	127	67, 72, 109, 193, 237
Benzidine [92-87-5]	23.87	184	92, 185
Trifluralin [1582-09-8]	23.88	306	43, 264, 41, 290
Bromoxynil [1689-84-5]	23.90	277	279, 88, 275, 168
Pyrene [129-00-0]	24.02	202	200, 203
Monocrotophos [6923-22-4]	24.08	127	192, 67, 97, 109
Phorate [298-02-2]	24.10	75	121, 97, 93, 260
Sulfallate [95-06-7]	24.23	188	88, 72, 60, 44
Demeton-S [126-75-0]	24.30	88	60, 81, 88, 114, 115
Phenacetin [62-44-2]	24.33	108	180, 179, 109, 137, 80
Dimethoate [60-51-5]	24.70	87	93, 125, 143, 229
Phenobarbital [50-06-6]	24.70	204	117, 232, 146, 161
Carbofuran [1563-66-2]	24.90	164	149, 131, 122
Octamethyl pyrophosphoramide [152-16-9]	24.95	135	44, 199, 286, 153, 243
4-Aminobiphenyl [92-67-1]	25.08	169	168, 170, 115
Dioxathion	25.25	97	125, 270, 153
Terbufos [13071-79-9]	25.35	231	57, 97, 153, 103
Dimethylphenylamine [122-09-8]	25.43	58	91, 66, 134, 42

(*Continued*)

TABLE 55.2 (*Continued*)
Semivolatile Organic Compounds and Their Retention Times and Characteristic Mass Ions (U.S. EPA Method 8270)

Compounds/CAS Number	RT (min)	Primary Mass Ion	Secondary Mass Ions
Pronamide [23950-58-5]	25.48	173	175, 145, 109, 147
Aminoazobenzene [60-09-3]	25.72	197	92, 120, 65, 77
Dichlone [117-80-6]	25.77	191	163, 226, 228, 135, 193
Dinoseb [88-85-7]	25.83	211	163, 147, 117, 240
Disulfoton [298-04-4]	25.83	88	97, 88, 142,186
Fluchloralin [33245-39-5]	25.88	306	63, 326, 328, 264, 65
Mexacarbate [315-18-4]	26.02	165	150, 134, 164, 222
4,4′-Oxydianiline [101-80-4]	26.08	200	108, 171, 80, 65
Butyl benzyl phthalate [85-68-7]	26.43	149	91, 206
4-Nitrobiphenyl [92-93-3]	26.55	199	152, 141, 169, 151
Phosphamidon [13171-21-6]	26.85	127	264, 72, 109, 138
2-Cyclohexyl-4,6-dinitrophenol [131-89-5]	26.87	231	185, 41, 193, 266
Methyl parathion [298-00-0]	27.03	109	125, 263, 79, 93
Carbaryl [63-25-2]	27.17	144	115, 118, 201
Dimethylaminoazobenzene [60-11-7]	27.50	225	120, 77, 105, 148, 42
Propylthiouracil [51-52-5]	27.68	170	142, 114, 83
Benz(a)anthracene [56-55-3]	27.83	228	229, 226
Chrysene-d_{12} (IS)	27.88	240	120, 236
3,3′-Dichlorobenzidine [91-94-1]	27.88	252	254, 126
Chrysene [218-01-9]	27.97	228	226, 229
Malathion [121-75-5]	28.08	173	125, 127, 93, 158
Kepone [143-50-0]	28.18	272	274, 237, 178, 143, 270
Fenthion [55-38-9]	28.37	278	125, 109, 169, 153
Parathion [56-38-2]	28.40	109	97, 291, 139, 155
Anilazine [101-05-3]	28.47	239	241, 143, 178, 89
Bis(2-ethylhexyl)phthalate [117-81-7]	28.47	149	167, 279
3,3-Dimethylbenzidine [119-93-7]	28.55	212	106, 198, 180
Carbophenothion [786-19-6]	28.58	157	97, 121, 342, 159, 198
5-Nitroacenaphthene [602-87-9]	28.73	199	152, 169, 141, 115
Methapyrilene [91-80-5]	28.77	97	50, 191, 71
Isodrin [465-73-6]	28.95	193	66, 195, 263, 265, 147
Captan [133-06-2]	29.47	79	149, 77, 119, 117
Chlorfenvinphos [470-90-6]	29.53	267	269, 323, 325, 295
Crotoxyphos [7700-17-6]	29.73	127	105, 193, 166
Phosmet [732-11-6]	30.03	160	77, 93, 317, 76
EPN [2104-64-5]	30.11	157	169, 185, 141, 323
Tetrachlorvinphos [961-11-5]	30.27	329	109, 331, 79, 333
Di-*n*-octyl phthalate [117-84-0]	30.48	149	167, 43
2-Aminoanthraquinone [117-79-3]	30.63	223	167, 195
Barban [101-27-9]	30.83	222	51, 87, 224, 257, 153
Aramite [140-57-8]	30.92	185	191, 318, 334, 197, 321
Benzo(b)fluoranthene [205-99-2]	31.45	252	253, 125
Nitrofen [1836-75-5]	31.47	283	285, 202, 139, 253
Benzo(k)fluoranthene [207-08-9]	31.55	252	253, 125
Chlorobenzilate [510-15-6]	31.77	251	139, 253, 111, 141

(*Continued*)

TABLE 55.2 (*Continued*)
Semivolatile Organic Compounds and Their Retention Times and Characteristic Mass Ions (U.S. EPA Method 8270)

Compounds/CAS Number	RT (min)	Primary Mass Ion	Secondary Mass Ions
Fensulfothion [115-90-2]	31.87	293	97, 308, 125, 292
Ethion [563-12-2]	32.08	231	97, 153, 125, 121
Diethylstilbestrol [56-53-1]	32.15	268	145, 107, 239, 121, 159
Famphur [52-85-7]	32.67	218	125, 93, 109, 217
Tri-*p*-tolyl phosphate [78-32-0]	32.75	368	367, 107, 165, 198
Benzo(a)pyrene [50-32-8]	32.80	252	253, 125
Perylene-d_{12} (IS)	33.05	264	260, 265
7,12-Dimethylbenz(a)anthracene [57-97-6]	33.25	256	241, 239, 129
5,5-Diphenylhydantoin [57-41-0]	33.40	180	104, 252, 223, 209
Captafol [2425-06-1]	33.47	79	77, 80, 107
Dinocap [39300-45-3]	33.47	69	41, 39
Methoxychlor [72-43-5]	33.55	227	228, 152, 114, 274, 212
2-Acetylaminofluorene [53-96-3]	33.58	181	180, 223, 152
4,4′-Methylenebis(2-chloroaniline) [101-14-4]	34.38	231	266, 268, 140, 195
3,3′-Dimethoxybenzidine [119-90-4]	34.47	244	201, 229
3-Methylcholanthrene [56-49-5]	35.07	268	252, 253, 126, 134, 113
Phosalone [2310-17-0]	35.23	182	184, 367, 121, 379
Azinphos methyl [86-50-0]	35.25	160	132, 93, 104, 105
Leptophos [21609-90-5]	35.28	171	377, 375, 77, 155, 379
Mirex [2385-85-5]	35.43	272	237, 274, 270, 239, 235
Tris(2,3-dibromopropyl) phosphate [126-72-7]	35.68	201	137, 119, 217, 219, 199
Dibenz(a,j)acridine [224-42-0]	36.40	279	280, 277, 250
Mestranol [72-33-3]	36.48	277	310, 174, 147, 242
Coumaphos [56-72-4]	37.08	362	226, 210, 364, 97, 109
Indeno(1,2,3-cd)pyrene [193-39-5]	39.52	276	138, 227
Dibenz(a,h)anthracene [53-70-3]	39.82	278	139, 279
Benzo(g,h,i)perylene [191-24-2]	41.43	276	138, 277
1,2:4,5-Dibenzopyrene [192-65-4]	41.60	302	151, 150, 300
Strychnine [57-24-9]	45.15	334	335, 333
Piperonyl sulfoxide [120-62-7]	46.43	162	135, 105, 77
Hexachlorophene [70-30-4]	47.98	196	198, 209, 211, 406, 408
Aldrin [309-00-2]		66	263, 220
Aroclor 1016 [12674-11-2]		222	260, 292
Aroclor 1221 [11104-28-2]		190	224, 260
Aroclor 1232 [11141-16-5]		190	224, 260
Aroclor 1242 [53469-21-9]		222	256, 292
Aroclor 1248 [12672-29-6]		292	362, 326
Aroclor 1254 [11097-69-1]		292	362, 326
Aroclor 1260 [11096-82-5]		360	362, 394
Alpha-BHC [319-84-6]		183	181, 109
Beta-BHC [319-85-7]		181	183, 109
Delta-BHC [319-86-8]		183	181, 109
Gamma-BHC (Lindane) [58-89-9]		183	181, 109
4,4′-DDD [72-54-8]		235	237, 165
4,4′-DDE [72-55-9]		246	248, 176

(*Continued*)

TABLE 55.2 (*Continued*)
Semivolatile Organic Compounds and Their Retention Times and Characteristic Mass Ions (U.S. EPA Method 8270)

Compounds/CAS Number	RT (min)	Primary Mass Ion	Secondary Mass Ions
4,4′-DDT [50-29-3]		235	237, 165
Dieldrin [60-57-1]		79	263, 279
1,2-Diphenylhydrazine [122-66-7]		77	105, 182
Endosulfan I [959-98-8]		195	339, 341
Endosulfan II [33213-65-9]		337	339, 341
Endosulfan sulfate [1031-07-8]		272	387, 422
Endrin [72-20-8]		263	82, 81
Endrin aldehyde [7421-93-4]		67	345, 250
Endrin ketone [53494-70-5]		317	67, 319
2-Fluorobiphenyl (surr) [321-60-8]		172	171
2-Fluorophenol (surr) [367-12-4]		112	64
Heptachlor [76-44-8]		100	272, 274
Heptachlor epoxide [1024-57-3]		353	355, 351
Nitrobenzene-d_5 (surr)		82	128, 54
N-Nitrosodimethylamine [62-75-9]		42	74, 44
Phenol-d_6 (surr)		99	42, 71
Terphenyl-d_{14} (surr)		244	122, 212
2,4,6-Tribromophenol (surr)		330	332, 141
Toxaphene [8001-35-2]		159	231, 233

Note: Surr, surrogate; IS, internal standard.

reduce ion-molecule reactions and can produce electron impact-like spectra and meet the DFTPP tuning criteria. When using an ion trap set the axial modulation, manifold temperature, and emission current to the manufacturer's recommendations. A computer data system should be interfaced to the mass spectrometer to allow the continuous acquisition and storage of mass spectra obtained throughout the duration of the chromatographic program. The computer should have the software to

TABLE 55.3
Ion Abundance Criteria for DFTPP (Bis(perfluorophenyl)phenyl Phosphine)

Mass (*m/z*)	Relative Abundance Criteria	Purpose of Checkpoint
51	10%–18% of the base peak	Low-mass sensitivity
68	<2% of mass 69	Low-mass resolution
70	<2% of mass 69	Low-mass resolution
127	10%–80% of the base peak	Low- to mid-mass sensitivity
197	<2% of mass 198	Mid-mass resolution
198	Base peak or >50% of mass 442	Mid-mass resolution and sensitivity
199	5%–9% of mass 198	Mid-mass resolution and isotope ratio
275	10%–60% of base peak	Mid- to high-mass sensitivity
365	>1% of the base peak	Baseline threshold
441	Present and < mass 443	High-mass resolution
442	Base peak or >50% of mass 198	High-mass resolution and sensitivity
443	15%–24% of mass 442	High-mass resolution and isotope ratio

integrate the abundances of the extracted ion current profile and be able to search compounds from the mass spectral library. The GC/MS conditions used in this method are summarized below and they should serve as guidance.

Mass range: 35–500 amu
Scan time: 1 s/scan
Initial temperature: 40°C, hold for 4 min
Temperature program: 40°C–270°C at 10°C/min
Final temperature: 270°C, hold until benzo[g,h,i]perylene elutes
Injector temperature: 250°C–300°C
Transfer line temperature: 250°C–300°C
Source temperature: as per manufacturer's specifications
Injector: Grob-type, split-less
Injection volume: 1–2 μL
Carrier gas: Hydrogen at 50 cm/s or helium at 30 cm/s
Ion trap only: follow the manufacturer's recommendations

U.S. EPA Method 8275. This method involves thermal extraction of the targeted compounds of PCBs and PAHs from soil, sediments, and solid waste and their analyses by capillary GC/MS procedure. There are 41 analytes listed under this method. Out of these, 18 compounds are polyaromatics containing two or more fused benzenoid rings and 19 are chlorinated biphenyls. The other analytes that are listed under this method, that are neither PCBs nor PAH congeners, are 4-bromophenyl phenyl ether, 1-chloronaphthalene, 1,2,4-trichlorobenzene, and hexachlorobenzene. In addition, several other substances not listed under this method may also be analyzed by this procedure.

A small portion of sample weighing between 0.003 and 0.250 g is weighed into a sample crucible. The crucible is then heated to 340°C in a thermal extraction chamber and held for 3 min. The compounds thermally extracted from the sample matrix are swept into a GC equipped with a split/split-less injection port. The split ratio set at about 35:1 for a low concentration sample and 400:1 for a high concentration sample and then concentrated on the head of the GC column. The thermal desorption time in this method is 13 min. The targeted compounds are analyzed by GC/MS.

U.S. EPA Method 625. This method describes an analytical procedure to detect and measure 72 semivolatile compounds in wastewater. The analytical steps are more or less similar to those of the Method 8270C discussed above. Out of these 72 compounds, 11 are acid extractable compounds while 61 are grouped under base/neutrals. In addition, this method lists an additional nine extractable substances that may be analyzed by this procedure. The terms, acid extractable and base/neutrals are based on the concept of acid–base partitioning of semivolatile organic compounds in aqueous samples subjected to LLE. The pH of the sample is adjusted to below 2 and above 10, respectively, with HCl and NaOH before extraction with methylene chloride. Such pH adjustment enables the acidic substances to separate from those that are basic or neutral and partition into a suitable water-immiscible organic solvent. Thus, when the pH of the aqueous sample is adjusted below 2 and then methylene chloride is added to the sample and the sample is shaken in a separatory funnel or swirled in a mechanical shaker, acidic substances such as phenols partition from the aqueous phase into the methylene chloride phase. Similarly, by adjusting the pH of the sample to above 10 enables the organic bases, such as amines or neutral compounds, including most pesticides and polynuclear aromatics to transfer from the aqueous phase into methylene chloride. The methylene chloride extracts of the samples are then concentrated down to a small volume usually to 1 mL using a Kuderna–Danish setup. Sample extracts may now be cleaned up further, if required, to remove the interfering substances that may mask the compounds of interest in the chromatogram. Since the compounds are identified and confirmed from their mass spectra, such cleanup steps may be avoided for relatively clean waters. Various extraction and cleanup procedures are discussed in several chapters in this text. The compounds present in the solvent extracts are separated on a GC

column, identified, and quantified by a mass spectrometer operating in the electron-impact ionization mode. In addition, the compounds can be measured alternatively under chemical ionization. The tuning substance for the mass spectrometer for this method is DFTPP. Thus, the abundances of all the characteristic mass ions of this compound must meet the tuning criteria that have been set for this method before commencing the analysis.

U.S. EPA Method 525.2. This method describes a procedure for the analysis of 118 compounds in potable waters. Unlike Method 625 that uses LLE and Method 8270 that describes several different types of extractions depending on the sample matrix, Method 525.2 employs a specific SPE, also known as LSE technique to extract a wide range of organic compounds from water. Such LSE methods also give a much lower limit of detection for the compounds present in the waters in comparison with the other two methods. The compounds in this method are partitioned from water samples onto a solid adsorbent composed of C_{18} (octadecyl) organic phase that is chemically bonded to a solid matrix using a disk or a cartridge.

The semivolatile or the nonvolatile organic analytes, internal standards, and surrogates are extracted from the water by passing 1 L of sample water through the cartridge or disk. The organic compounds are eluted from the LSE cartridge or disk with small quantities of ethyl acetate followed by methylene chloride. The extract is concentrated further by evaporation of some of the solvent. The compounds in the extract are separated, identified, and measured by injecting an aliquot of the concentrated extract into a high-resolution fused silica capillary column of a GC/MS system. Compounds are identified by comparing their measured mass spectra and their retention times to the reference spectra and their retention times in a database obtained by measuring their calibration standards under the same conditions used for the samples. The concentrations of analytes and surrogates are measured by the same internal standard calibration procedure.

LSE cartridges are available from several commercial suppliers. These are to be of plastic, such as polypropylene or from glass and must not contain plasticizers, such as phthalates or adipates that could leach into the eluting solvents, ethyl acetate, and methylene chloride. The cartridges are packed with about 1 g of silica or other inorganic support, chemically bonded to octadecyl (C_{18}) groups. The packing must have a narrow size distribution and must not leach organic compounds into the eluting solvent. One liter of water should pass through the cartridge in about 2 h under low vacuum of about 13 cm (5 in.). If extraction disks are to be used, they have to be packed with octadecyl-bonded silica uniformly enmeshed in an inert matrix. The diameter and thickness of the disk used to generate data in this method was 47 and 0.5 mm, respectively. Other disk sizes, however, may be employed if needed. The packing in the disk should allow the passage of 1 L of water in 5–20 min under a vacuum of 66 cm (26 in.) mercury. As with the cartridges, the disks should not contain any organic compounds from either the matrix or the bonded silica, such as phthalates or adipates that will leach into the eluting solvents, ethyl acetate, and methylene chloride.

The sample extraction procedure may be carried out either in the manual mode or in the automated mode. Follow the manufacturer's operating instructions when using an automatic sample preparation device. For manual cartridge extraction, elute each cartridge with 5 mL aliquots of ethyl acetate and then methylene chloride. Allow the cartridge to drain dry after each flush. Then, elute the cartridge with a 10 mL aliquot of methanol. Do not allow the methanol to elute below the top of the cartridge packing nor let the cartridge go dry. Add 10 mL of reagent water to the cartridge. Before the reagent water level drops below the top edge of packing, begin adding the sample to the solvent reservoir. Pour the water sample into the 2 L separatory funnel with the stopcock closed, add 5 mL of methanol, and mix well. Add 100 μL aliquot of internal standards and surrogate solutions to the sample. The final concentrations of these internal standards and the surrogates should be 5 μg/L. Pass the sample through the cartridge. If a vacuum manifold is used instead of the separatory funnel, the sample may be transferred directly to the cartridge after the methanol is added to the sample. It may be noted here that the sample must not contain any residual chlorine and its pH should be about 2. The procedure for the disk extraction is more or less the same as the cartridge extraction. After the entire sample has been passed through the LSE cartridge or the disk, draw

air or nitrogen through the cartridge or disk for 10 min. The cartridge or disk is eluted with 5 mL aliquot each of ethyl acetate and methylene chloride and the eluate is collected in a collection tube. It is then passed through a drying column packed with anhydrous sodium sulfate for the removal of the trace water. Wash the sodium sulfate with a small amount of methylene chloride. The eluate and the methylene chloride washing is collected in a second vial and concentrated down to a small volume in a warm water bath under a gentle stream of nitrogen. The final volume of the sample extract is adjusted to the desired volume with ethyl acetate. The volume of the extract should not be concentrated to below 0.5 mL, as this may result in losses of the analytes.

A 1 μL aliquot of the sample extract is injected into the GC/MS for analysis. The compounds are identified by comparison of their mass spectra and their GC retention times to their reference spectra and their retention times in the user-created database. The GC retention time of the sample component should be within 5 s of the retention time observed for that compound in the most recently analyzed continuing calibration check standard. The analytes and surrogate concentrations are calculated as follows from their multipoint calibration standards using the internal standard method.

$$C_x = \frac{(A_x)(Q_{is})}{(A_{is})(\mathrm{RF})(V)}$$

where

C_x is the concentration of the analyte or surrogate in μg/L in the water sample
A_x is the integrated abundance of the quantitation ion of the analyte in the sample
A_{is} is the integrated abundance of the quantitation ion of the internal standard in the sample
Q_{is} is the total quantity (in micrograms) of the internal standard added to the water sample
V is the volume of the original water sample (L)
RF is the mean response factor of the analyte from the initial calibration. RF is a unit-less value and is calculated as $(A_x)(Q_{is})/(A_{is})(Q_x)$, where Q_x is the abundance of the quantitation ion of the internal standard

Concentrations of the compounds should be rounded to three significant figures above 99 μg/L, two significant figures for the concentrations between 1 and 99 μg/L, and one significant figure for the lower concentrations.

Some of the organic compounds listed under this method may coelute under the conditions of the analysis. The mass spectra of each analyte spectrum should be carefully examined to identify the compounds. Structural isomers that produce very similar mass spectra may be identified only if they have sufficiently different GC retention times. Resolution of such isomers may be considered acceptable if the height of the valley between the two isomer peaks is less than 25% of the average of the average height of the two peak heights. If such resolution cannot be achieved the structural isomers are then identified as isomeric pairs. An example of one such isomeric pair is benzo[b]- and benzo[k]fluoranthene. A multicomponent analyte, such as toxaphene or Aroclor can be identified by the presence of its individual components in a characteristic pattern based on the relative amounts of each component present.

U.S. EPA Method 526. This method gives an analytical procedure to determine 11 selected semivolatile organic compounds in drinking water by SPE and capillary column GC/MS. This method is quite similar to the Method 525 discussed above. A 1 L water sample is passed through a SPE disk or cartridge containing polystyrenedivinylbenzene (SDVB) cartridge to extract the target analytes and surrogate compounds. The extract is dried by passing through a column of anhydrous sodium sulfate and is concentrated by blowdown with nitrogen to a volume of about 0.7 mL. Internal standards are added and the extract is diluted to a final volume of 1 mL and analyzed by GC/MS.

Standard Method 6410. This method under the title "Extractable Base/Neutrals and Acids" is adapted from U.S. EPA Method 625. This is a broad-spectrum GC/MS packed- or capillary-column

TABLE 55.4
Characteristic Masses for Extractable Base/Neutrals and Acids under the Chemical Ionization (Methane) Conditions (SM Method 6410)

Compounds	Characteristic Masses
Extractable Base/Neutrals	
1,3-Dichlorobenzene	146, 148, 150
1,4-Dichlorobenzene	146, 148, 150
Hexachloroethane	199, 201, 203
Bis(2-chloroethyl)ether	63, 107, 109
1,2-Dichlorobenzene	146, 148, 150
Bis(2-chloroisopropyl)ether	77, 135, 137
Nitrobenzene	124, 152, 164
Hexachlorobutadiene	223, 225, 227
1,2,4-Trichlorobenzene	181, 183, 209
Isophorone	139, 167, 178
Naphthalene	129, 157, 169
Bis(2-chloroethoxy) methane	65, 107, 137
Hexachlorocyclopentadiene	235, 237, 239
2-Chloronaphthalene	163, 191, 203
Acenaphthylene	152, 153, 181
Acenaphthene	154, 155, 183
Dimethyl phthalate	151, 163, 164
2,6-Dinitrotoluene	183, 211, 223
Fluorene	166, 167, 195
2,4-Dinitrotoluene	183, 211, 223
Diethyl phthalate	177, 223, 251
N-Nitrosodiphenylamine	169, 170, 198
Hexachlorobenzene	284, 286, 288
4-Bromophenyl phenyl ether	249, 251, 277
Phenanthrene	178, 179, 207
Anthracene	178, 179, 207
Dibutyl phthalate	149, 205, 279
Fluoranthene	203, 231, 243
Pyrene	203, 231, 243
Benzidine	185, 213, 225
Butyl benzyl phthalate	149, 299, 327
Bis(2-ethylhexyl) phthalate	149
Chrysene	228, 229, 257
Benzo(a)anthracene	228, 229, 257
Benzo(b)fluoranthene	252, 253, 281
Benzo(k)fluoranthene	252, 253, 281
Benzo(a)pyrene	252, 253, 281
Indeno(1,2,3-cd)pyrene	276, 277, 305
Dibenzo(a,h)anthracene	278, 279, 307
Benzo(ghi)perylene	276, 277, 305
Acid extractables	
2-Chlorophenol	129, 131, 157
2-Nitrophenol	140, 168, 122
Phenol	95, 123, 135

(*Continued*)

TABLE 55.4 (*Continued*)
Characteristic Masses for Extractable Base/Neutrals and Acids under the Chemical Ionization (Methane) Conditions (SM Method 6410)

Compounds	Characteristic Masses
2,4-Dimethylphenol	123, 151, 163
2,4-Dichlorophenol	163, 165, 167
2,4,6-Trichlorophenol	197, 199, 201
4-Chloro-3-methylphenol	143, 171, 183
2,4-Dinitrophenol	185, 213, 225
2-Methyl-4,6-dinitrophenol	199, 227, 239
Pentachlorophenol	267, 265, 269
4-Nitrophenol	140, 168, 122

method for detecting semivolatile compounds following LLE. The GC chromatograms of the base/neutrals and the acid fractions, the retention times, and the characteristic masses of the compounds along with their MDLs are presented in this method. Also given in this method are the QC acceptance criteria for all these compounds along with the statistical method bias and the overall precision in analysis as a function of the concentrations of the analytes. The characteristic mass ions for all the analytes of this method under the electron-impact ionization mode are given along with the mass ions of a number of compounds that too are produced in the chemical ionization mode. Presented in Table 55.4 are the characteristic masses of such compounds produced when analyzed under the chemical ionization mode, whereas Table 55.2 presents the mass ions produced under electron impact ionization of all compounds that are listed under the Method 8270. All the base/neutrals and the acid extractable compounds in Table 55.2 are listed in the order of their increasing retention times respectively and not alphabetically. It may be noted here that several compounds that are isomers show the same characteristic masses and such substances therefore should be distinguished by their retention times. Readers may refer to this method for the details of the analytical procedure, QC, and all other pertinent information on the analysis of such compounds in water.

SAMPLING AND STORAGE

The grab samples are collected in 1 L amber glass bottles fitted with TFE screw caps. Foils may be used instead of the TFE if the sample is not corrosive. Samples should be protected from light if amber bottles are not used. Store samples at 4°C from the time of collection until they are extracted. If residual chlorine is present in the sample, add 80 mg of sodium thiosulfate per liter of the sample and mix well. Samples must be extracted within 7 days of collection and analyzed within 40 days of extraction.

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56 Silica

Silica (SiO_2) occurs in high abundance all over the earth. It occurs in the form of sand and quartz. It is also present in rocks and silicate minerals. It is found in natural waters at varying concentrations from 1 to 100 mg/L.

Silica in water may be analyzed by the following methods:

1. Gravimetric method
2. Ammonium molybdate colorimetric method
3. Atomic absorption spectrophotometric method

Methods 1 and 2 are presented below. Method 3 is discussed in brief under metal analysis.

GRAVIMETRIC METHOD

Silica and silicates (SiO_3^{2-} and SiO_4^{4-}) react with hydrochloric or perchloric acid to form silicic acid, H_2SiO_3. The evaporation of the solution precipitates dehydrated silica. Upon ignition, dehydration is completed. The reaction steps are summarized below:

$$SiO_2 \text{ or silicates} \xrightarrow{HCl/HClO_3} H_2SiO_3$$

$$\xrightarrow{\text{evaporation}} \text{partially dehydrated } SiO_2$$

$$\xrightarrow[\text{at } 1200^\circ C]{HCl/HClO_3} SiO_2 + H_2O \uparrow$$

The residue after ignition is weighed along with its container. This residue consists of dehydrated silica plus any nonvolatile impurities in the sample. Hydrofluoric acid is then added to this residue. This converts all silica in the residue to silicon tetrafluoride, SiF_4, as shown below:

$$SiO_4 + 4HF \rightarrow SiF_4 + 2H_2O$$

Upon ignition, SiF_4 volatilizes leaving behind any nonvolatile impurities. The container is coded and weighed again. The difference in weight is equal to the amount of silica that volatilizes.

$$\text{mg } SiO_2/\text{L} = \frac{(W_1 - W_2) \times 1000}{\text{mL sample taken}}$$

where

W_1 is the weight of the crucible and contents before HF treatment

W_2 is the weight of the crucible and contents after volatilization of SiF_4

Procedure

Place 100–200 mL of sample in a platinum evaporating dish (or an acid-leached glazed porcelain dish without etching). Add 5 mL of 1:1 HCl. Evaporate to near dryness in a 110°C oven or on a hot plate. Add another 5 mL 1:1 HCl. Evaporate to dryness. Add a small volume of 1:50 hot HCl and rinse the residue. Filter the mixture through an ashless filter paper. Transfer the entire residue quantitatively

from the 110°C evaporating dish onto the filter paper using distilled water. Wash the residue several times with diluted water until the washings show no chlorine ion (test with $AgNO_3$; the addition of a few drops of $AgNO_3$ reagent to the washing should not produce white precipitate or turbidity).

Transfer the filter paper and residue to a platinum crucible. Dry at 110°C. Heat the covered crucible (keeping a little opening) gradually to 1200°C. Cool in a desiccator and weigh. Repeat the ignition, cooling, and weighing until constant weight is attained.

Moisten the residue with distilled water. Add a few drops of 1:1 H_2SO_4 followed by 10 mL HF (48% strength). Evaporate the mixture slowly to dryness. Ignite the residue at 1200°C. Record the constant weight. Determine the concentration of dissolved silica in the sample from the above equation.

AMMONIUM MOLYBDATE COLORIMETRIC METHOD

Under acid condition (at pH∼1) silica reacts with ammonium molybdate to form a yellow colored heteropoly acid, silicomolybdic acid. The reactions are shown below:

$$SiO_2 + H_2O \Rightarrow H_2SiO_3$$
(silicic acid)

$$H_2SiO_3 + 3H_2O \Rightarrow H_8SiO_6$$
(silicic acid hydrate)

$$H_8SiO_6 + 12NH_4MoO_4 + 12H_2SO_4$$
(ammonium molybdate)

$$\Rightarrow H_8[Si(Mo_2O_7)_6] + 12NH_4SO_4 + 12H_2O$$
(silicomolybdic acid)

Phosphate reacts with ammonium molybdate too, similarly forming yellow phosphomolybdic acid. The presence of phosphate, therefore, interferes in the test. The addition of oxalic acid or citric acid destroys phosphomolybdic acid complex but not silicomolybdic acid complex. The intensity of color developed is proportional to the concentration of silica in the sample.

An additional color development step may often be required to confirm the yellow color of silicomolybdic acid. The latter is reduced to a dark blue substance by treating with aminonaphthalene sulfonic acid. The color of heteropoly blue formed is more intense than the yellow color of silicomolybdic acid. The latter test is more sensitive and can give a detection limit of 50 μg silica/L when using a spectrophotometer.

Certain forms of silica and many polymeric silicates do not react with ammonium molybdate. These complex silicates may be decomposed to simple molybdatereactive silica by high-temperature digestion or fusion with sodium bicarbonate.

Procedure

Place 50 mL of sample in a Nessler tube. Add 1 mL of 1:1 HCl and 2 mL ammonium molybdate reagent. Shake well. Let the solution stand for 5 min. Add 2 mL oxalic acid solution, shake thoroughly, and allow the solution to stand for another 5 min. Measure the absorbance of the yellow color developed at 410 nm. Run a blank using 50 mL distilled water following the above procedure. Compare the absorbance of the sample solution with the standards and determine the concentration of silica from the calibration curve.

As a more sensitive alternative test or an additional confirmatory test, add 2 mL of aminosulfonic acid reducing reagent 5 min after adding oxalic acid solution. Let the solution stand for 5 min and then measure the absorbance at 815 or 650 nm (at the latter wavelength the sensitivity is reduced.) Plot a separate calibration curve. Read the concentration of analyte from the calibration curve.

Reagent

- Reducing agent: to 300 mL of $NaHSO_3$ solution (~20% strength), add 100 mL of solution containing 1 g 1-amino-2-naphthol-4-sulfonic acid and 2 g Na_2SO_3. Filter and store the reagent in a plastic bottle in the dark at 4°C. Discard this solution when it becomes dark.

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57 Sulfate

Sulfate is a divalent polyanion having the formula SO_4^{2-}. It is a common contaminant, occurring widely in wastewater, waste, and potable water. The sulfate in water may be analyzed by

1. Ion chromatography
2. Gravimetric method
3. Turbidimetric method

Method 1 is suitable for measuring low concentrations of SO_4^{2-}, at less than 1 ppm level. The lower limit of detection is about 0.1 mg/L. The gravimetric method, on the other hand, is reliable only at a relatively high concentration range (>10 mg/L). The turbidimetric method is applicable in the concentration range of 1–40 mg/L. Samples with high SO_4^{2-} concentrations may be accordingly diluted prior to analysis.

GRAVIMETRIC METHOD

Sulfate is precipitated as barium sulfate when added to barium chloride solution. The reaction is shown below for sodium sulfate:

$$Na_2SO_4 + BaCl_2 \rightarrow 2NaCl + BaSO_4$$

The reaction is performed at boiling temperature and in the HCl medium. An acid medium is required to prevent any precipitation of $BaCO_3$ and $Ba_3(PO_4)_2$.

The precipitate is filtered, washed free from Cl^-, dried, and then weighed. Alternately, the precipitate, along with the filter paper, is ignited in a platinum crucible at 800°C. $BaSO_4$ residue is weighed and SO_4^{2-} concentration is calculated.

Interference

Silica and suspended matter in the sample produce high results, as does NO_3^-, which forms $Ba(NO_3)_2$ and is occluded with $BaSO_4$ precipitate. Heavy metals interfere in the test by precipitating as sulfates, thus giving low results. Sulfates and bisulfates of alkali metals may occlude with $BaSO_4$, yielding low results.

Procedure

A measured volume of sample is evaporated nearly to dryness in a platinum dish and then treated with 1–2 mL of HCl. Evaporation is continued. The sample residue is successively treated with HCl and evaporated. The aim is to extract the SO_4^{2-} leaving behind the insoluble silica and suspended matter in the residue. The residue is then heated with distilled water and the washing is combined with the acid solution.

The pH of the clear filtrate solution free from silica and suspended matters is now adjusted to 4.5–5.0. The solution is heated. $BaCl_2$ solution is slowly added with stirring until precipitation is complete.

The precipitate, $BaSO_4$, is filtered through a fritted glass filter (pore size <5 μm) or a 0.45 μm membrane filter. It is washed a few times with small amounts of hot distilled water to remove any Cl^- ion that may be adhering to it. It is dried in an oven for several hours at 105°C, cooled in a desiccator, and weighed. Heating, cooling, and weighing are repeated until a constant weight is obtained.

Alternately, $BaSO_4$ precipitate along with the filter paper is placed in a weighed platinum crucible and ignited at 800°C for 1–2 h. It is then cooled in a desiccator and weighed.

Calculation

$$\text{mg } SO_4^{2-}/\text{L} = \frac{\text{mg } BaSO_4 \times 0.4115}{\text{mL sample}}$$

The factor 0.4115 comes from the ratio of formula weight of SO_4^{2-} to that of $BaSO_4$, which is 96.04/233.40.

TURBIDIMETRIC METHOD

Sulfate ion is precipitated as $BaSO_4$ in an acid medium, reacting with $BaCl_2$. The solution turns turbid due to white $BaSO_4$ precipitate. The turbidity is measured by a nephelometer. Alternatively, the light absorbance of the $BaSO_4$ suspension is measured at 420 nm by a spectrophotometer providing a light path of 2.5–10 cm. A filter photometer equipped with a violet filter may also be used to measure the light transmittance at 420 nm. The concentration of SO_4^{2-} in the sample is determined from a standard calibration curve.

Turbidimetric method is applicable when the SO_4^{2-} concentrations is between 5 and 50 mg/L. For concentrations above 50 mg/L, dilute the sample and analyze.

The presence of a large amount of suspended matter or color in the sample would interfere in the test. Filter the sample to remove suspended matter.

Procedure

To a 100 mL sample, add 5 mL conditioning reagent. Stir the solution and add a spoonful of $BaCl_2$ crystals. Stir it for a minute at a constant speed. Measure the turbidity of this solution.

Prepare a calibration curve by plotting turbidity (in NTU if a nephelometer is used), absorbance, or transmittance (if a spectrophotometer or filter photometer is used) of $BaSO_4$ formed against the corresponding concentrations of SO_4^{2-} standards. Determine the concentration of SO_4^{2-} in the sample from the standard calibration curve.

Calculation

$$\text{mg } SO_4^{2-}/\text{L} = \frac{\text{mg } SO_4^{2-} \text{ read from the calibration curve} \times 1000}{\text{mL sample}}$$

Reagents

Conditioning agent: mix 30 mL conc. HCl, 300 mL distilled water, 100 mL 95% ethanol, and 75 g NaCl in a container. Add 50 mL glycerol and mix.

Sulfate standards: dissolve 147.9 mg anhydrous Na_2SO_4 in 1 L distilled water. Concentration of this stock solution is 100 mg SO_4^{2-}/L. Prepare five calibration standards from this stock solution as follows:

Dilution	Concentration, mg/L
2 mL → 100 mL	2.0
5 mL → 100 mL	5.0
10 mL → 100 mL	10.0
20 mL → 100 mL	20.0
40 mL → 100 mL	40.0

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58 Sulfide

Sulfide (S^{2-}) is a bivalent monoanion produced from the decomposition of metal sulfide salts. It occurs in groundwater, hot springs, and wastewater. It is also formed from the bacterial reduction of sulfate. Sulfide salts in solid waste in contact with an acid can produce hydrogen sulfide, H_2S, which is highly toxic. In an aqueous sample, sulfide may be present as dissolved H_2S and HS^-, dissolved metallic sulfide, and acid-soluble metallic sulfide contained in suspended particles. All these soluble and insoluble sulfides and dissolved H_2S and HS^- together are termed as total sulfide. The sulfide remaining after the removal of suspended solids is termed the dissolved sulfide. Copper and silver sulfides are insoluble even under acidic conditions. Therefore, these two sulfides are not determined in the following tests.

In a nonaqueous sample, such as soil, sediment, or hazardous waste, the sample is vigorously shaken with acidified water to leach out the sulfide. Sulfide in aqueous samples or leachates may be analyzed by one of the following methods:

1. Iodometric method
2. Methylene blue colorimetric method
3. Silver–silver sulfide electrode method

Methods 1 and 2 are commonly used in environmental analysis. Method 3 uses a silver electrode to indicate the end point of the potentiometric titration of dissolved sulfide with standard $AgNO_3$. The electrode response is slow.

ANALYSIS OF SULFIDE IN WATER (SEE FIGURE 58.1)

Screening Test for Sulfide

Before the analysis, it is often useful to determine qualitatively the presence of sulfide in the sample and the concentration range at which it is present. The following tests may be performed:

1. *Antimony test.* To 100 mL of sample, add five drops of saturated solution of potassium antimony tartrate and 5–10 drops of 6 N HCl. A yellow antimony sulfide formation would confirm the presence of sulfide. Perform this test with known standards to match the color intensity to determine the concentrations of sulfide in the sample. The test is sensitive to a concentration above 0.5 mg S^{2-}/L. Lead interferes in this test.
2. *Silver foil test.* H_2S evolved from a slightly acidified sample can blacken a strip of silver foil due to the formation of silver sulfide. Silver is cleaned by dipping in NaCN solution prior to exposure.
3. *Lead acetate paper test.* A paper moistened with lead acetate solution turns black due to the formation of lead sulfide on exposure to H_2S.

SAMPLE PRETREATMENT

Sample pretreatment, although not always necessary, should be performed prior to analysis. This is required to remove the interfering substances and also to concentrate the sample. The presence of reducing agents such as sulfite, thiosulfate, iodide, and many organic substances interfere with both

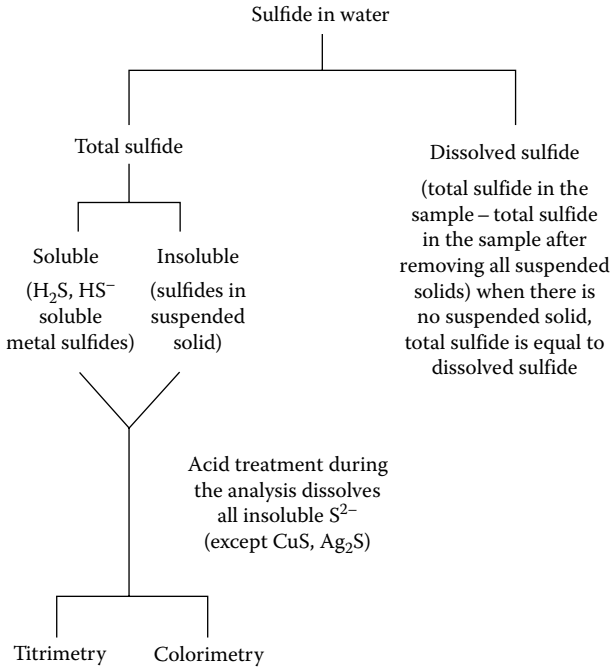


FIGURE 58.1 Analysis of sulfide in water.

the iodometric and methylene blue methods. The addition of a zinc or cadmium salt to the sample precipitates out the sulfide that settles at the bottom. The supernatant liquid containing the interfering substances is removed and is replaced with a smaller volume of distilled water to concentrate the sulfide. If sulfide concentration in the sample is found to be high from the antimony-screening test, do not concentrate. The supernatant liquid is removed and replaced by an equal volume of distilled water or a larger volume of water if dilution is required. Zinc sulfide precipitate, which is insoluble in water, dissolves after adding acid in the analysis.

Select a sample volume of 100 mL for the colorimetric test or 400 mL for the iodometric test. Add a few drops of zinc acetate solution (10% strength) into the flask and fill it with the sample. Add a few drops of 6 N NaOH solution to produce a pH above 9. Mix the solution vigorously using a shaker. If sulfide is present in the sample, it will form a precipitate. Allow the solution to stand for 15–20 min to let the precipitate settle. Decant and discard the supernatant liquid. Add a measured volume of distilled water. Note the final volume of solution containing the precipitate. Begin analysis immediately.

ANALYSIS OF DISSOLVED SULFIDE IN WATER

Analyze one aliquot of the sample for total sulfide by the iodide titrimetric or the methylene blue colorimetric test (discussed in detail in the following sections).

Suspended solids are removed from the other aliquot of the sample as follows. Add 1 mL of 6 N NaOH to a 500 mL glass bottle. Fill the bottle with the sample. Add 1 mL of $AlCl_3$ solution (10 g $AlCl_3 \cdot 6H_2O$ in 15 mL water). Stopper the bottle. Rotate the bottle back and forth for 2 min to flocculate the contents. Allow the contents to settle for 10–15 min. Draw out the supernatant liquid to analyze sulfide. The difference in the sulfide values obtained from both the tests (i.e., before and after removing suspended solids from the sample), is equal to the concentration of dissolved sulfide.

IODOMETRIC METHOD

An excess amount of iodine is added to the sample that may or may not have been treated with zinc acetate. Iodine oxidizes sulfide to sulfur under acidic condition. This is shown in the following equations:

$$I^2 + S^{2-} \xrightarrow{\text{acid}} S + 2I^-$$

or

$$I^2 + ZnS \xrightarrow{\text{acid}} S + ZnI^2$$

excess iodine (unreacted surplus iodine) is back titrated with standard sodium thiosulfate solution using starch indicator. PAO may be used as a titrant instead of sodium thiosulfate.

Procedure

A measured amount of standard iodine solution is placed in a 500 mL flask. The amount of iodine should be the excess over the expected quantity of sulfide in the sample. Add distilled water and bring the volume to 20 mL. Add 2 mL of 6 N HCl. Pipette 200 mL of sample into the flask. If the sulfide in the sample was precipitated as ZnS, transfer the precipitate with 100 mL distilled water into the flask. Add iodide solution and HCl. If iodine color disappears, add more iodine standard solution into the flask, until the color remains. Titrate with $Na_2S_2O_3$ standard. Before the end point, when the color changes to straw yellow or brown, add a few mL of starch solution and continue titration by the drop-wise addition of $Na_2S_2O_3$ standard until the blue color disappears. Record the volume of titrant added.

Calculation

$$\text{mg/L sulfide} = \frac{[(A \times B) - (C \times D) \times 16{,}000}{\text{mL sample}}$$

A is the mL of the standard iodine solution
B is the normality of the iodine solution
C is the mL of the titrant, $Na_2S_2O_3$ solution
D is the normality of the $Na_2S_2O_3$ solution

(Since S^{2-} has two negative charges, its equivalent weight is 32/2 or 16.) Equivalent weight expressed in mg, therefore, is 16,000, used in the above calculation.

If the normality of the standard iodine and standard $Na_2S_2O_3$ solutions are both 0.025, the above expression can be written as

$$\text{mg/L sulfide} = \frac{(A - C) \times 16{,}000 \times 0.025}{\text{mL of sample}}$$
$$= \frac{(A - C) \times 400}{\text{mL of sample}}$$

In other words, 1 L of 0.025 N standard iodine solution would react with 400 mg of sulfide. This may also be calculated from the following equation:

$$\underset{254\,\text{g}}{I_2} + \underset{32\,\text{g}}{S^{2-}} \Rightarrow \underset{254\,\text{g}}{S} + \underset{32\,\text{g}}{2I^-}$$

254 g I_2 reacts with 32 g S^{2-}. Therefore, 3.2 g I_2 weighed to make 0.025 N solution, would react with (32 g × 3.2 g)/254 g or 0.4 g or 400 mg of sulfide.

PAO may also be used as the reducing agent in the titration, instead of sodium thiosulfate.

Reagents

Standard iodine solution, 0.025 N: dissolve 20–25 g of KI in a small amount of water. Add 3.2 g of iodine and dissolve. Dilute with distilled water to 1 L. Standardize against 0.025 N $Na_2S_2O_3$ solution using starch indicator. In the equation, $I_2 + 2S_2O_3^{2-} \cdot 2I^- + S_4O_6^{2-}$, 1 g equivalent weight of iodine reacts with 1 g equivalent weight of $Na_2S_2O_3$. Therefore, the normality of standard iodine solution

$$= \frac{\text{mL of } Na_2S_2O_3 \text{ titrant} \times \text{Its normality}}{\text{mL of iodine solution in titration}}$$

Preparation and standardization of sodium thiosulfate/PAO solution: 0.025 M: dissolve 6.205 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) or 4.200 g of PAO (C_6H_5 AsO) in distilled water. Add 0.5 g of NaOH solid and dilute to 1 L. Standardize against potassium bi-iodate (potassium hydrogen iodate) solution as described below.

To 2 g of KI in 100 mL distilled water, add a few drops of conc. H_2SO_4. Add 25 mL of standard bi-iodate solution. Dilute to 200 mL and titrate the liberated iodine against thiosulfate or PAO using starch indicator.

The strength (molarity) of the titrant thiosulfate or PAO solution

$$= \frac{\text{Molarity of bi-iodate soln.} \times 12 \times 25\,\text{mL}}{\text{mL of titrant}}$$

$$= \frac{0.0021\,\text{M} \times 12 \times 25\,\text{mL}}{\text{mL of titrant}}$$

In the above calculation, the numerator is multiplied by 12, because 1 mol of bi-iodate = 12 mol of $S_2O_3^{2-}$ or PAO as determined from the following equation:

$$KH(IO_3)_2 + 10KI + 6H_2SO_4 \Rightarrow 6I_2 + 6H_2O + 5K_2SO_4 + KHSO_4$$

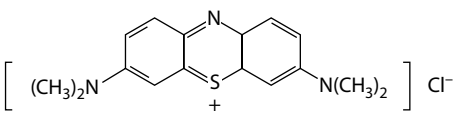
$$6I_2 + 12S_2O_3^{2-} \Rightarrow 12I^- + 6S_4O_6^{2-}$$

$$6I_2 + 12AsO^{2-} \Rightarrow 12I^- + 6As_2O_2^{2-}$$

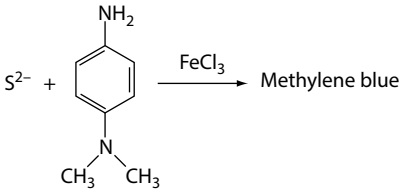
Standard potassium bi-iodate, $KH(IO_3)_2$, solution, 0.00208 M. The strength of potassium bi-iodate should be 0.025 M/12 or 0.00208 M. This is calculated from the thiosulfate strength 0.025 M and the following stoichiometry: 1 mol of thiosulfate + 1/12 mol of bi-iodate. Dissolve 0.8125 g $KH(IO_3)_2$ in distilled water and dilute to 1 L.

METHYLENE BLUE COLORIMETRIC METHOD

Methylene blue is a dye intermediate that is also used as an oxidation–reduction indicator. Its molecular formula in the trihydrate form is $C_{16}H_{18}N_3SCl \cdot 3H_2O$. It is soluble in water, forming a deep blue solution. The structure of methylene blue is as follows:



Sulfide reacts with *N,N*-dimethyl-*p*-phenylenediamine (*p*-aminodimethyl aniline) in the presence of ferric chloride to produce methylene blue:



The intensity of color developed is proportional to the concentration of sulfide in the sample. Color comparison may be done visually with methylene blue standard (sulfide equivalent). Alternatively, a spectrophotometer or a filter photometer may be used and the concentration of sulfide determined from a standard calibration curve. The color is measured at a wavelength maximum of 625 nm.

Procedure

Mark two matched test tubes as A and B and transfer 7.5 mL of the sample to each. To tube A, add 0.5 mL of amine–sulfuric acid reagent and three drops of $FeCl_3$ solution. Invert it once and mix the solution. If sulfide is present, the color of the solution develops to blue within a few minutes. Allow the solution to stand for 5 min. After this, add 2 mL of diammonium hydrogen-phosphate solution.

To test tube B containing an equal amount of sample, add 0.5 mL of 1:1 H_2SO_4, three drops of $FeCl_3$ solution, and invert once. After 5 min, add 2 mL of $(NH_4)_2HPO_4$ solution. Add 1:1 H_2SO_4 acid instead of the amine–sulfuric acid to the sample in tube B. Therefore, in this case, without the amine reactant, no methylene blue formation would occur. Add $(NH_4)_2HPO_4$ after 5 min. For photometric color comparison, use a 1 cm cell for 0.1–2.0 mg/L and a 10 cm cell for 2.0–20.0 mg/L of sulfide concentration. Zero the instrument with a sample portion from tube B, and read the absorbance of tube A. Plot a calibration curve between the sulfide concentration and the absorbance (see below) and determine the concentration of the sulfide in the sample from the graph.

If the color comparison is done visually, proceed as described below.

If the sulfide concentration in the sample is expected to be high or found to be high from qualitative testing, use methylene blue standard solution I. Otherwise, for a low concentration, use a diluted solution of this standard, methylene blue solution II. Add methylene blue solution(s) dropwise to tube B until the color matches to that developed in tube A. For high concentrations, start with a dropwise addition of solution I. When the color is close to matching, add solution II dropwise.

$$\text{Concentration of sulfide, mg/L} = \left(A + \frac{B}{10}\right) \times C$$

A is the number of drops of methylene blue solution I
B is the number of drops of methylene blue solution II
C is the conc. sulfide (mg/L) equivalent to one drop of methylene

METHYLENE BLUE SOLUTION: PREPARATION AND STANDARDIZATION

Solution I is made by dissolving 1.0 g of powder having a dye content certified as 84% or more in 1 L of distilled water. This solution should be standardized against the sulfide solution of known strength to determine the mg/L of sulfide that would react with one drop (0.05 mL) of the solution. Solution II is 1:10 dilution of solution I.

Standardization

Dissolve an accurately weighed 15.0 g of sodium sulfide ($Na_2S \cdot 9H_2O$) in 50–60 mL distilled water in a 100 mL volumetric flask. Dilute to the mark. Add one drop of this solution (0.05 mL) to 1 L of distilled water in a volumetric flask. Shake well. That makes the concentration of the solution as 1 mg S^{2-}/L (1 ppm). Prepare five calibration standards in the range 1–10 mg S^{2-}/L using 1–10 drops of the stock solution. To a 7.5 mL aliquot of each standard, add the reagents and follow the procedure described above under colorimetric method. Read the absorbance of the color developed at 625 nm and draw a standard calibration curve plotting the absorbance versus concentration of sulfide.

If color comparison is made visually, standardize the methylene blue solution I or II as described below.

Match the color developed in one of the sulfide standard aliquots (after adding the reagents) to that of methylene blue solution, either by diluting the latter, or by adding more dye. For example, select the 1 ppm sulfide standard and match the color developed in it with the color of the prepared methylene blue solution I.

7.5 mL of 1 mg/L sulfide standard + 7.5 μg of S^{2-} that would react with 63.8 μg *N,N*-dimethyl-*p*-phenylenediamine in the presence of $FeCl_3$ to produce 75 μg of methylene blue ($C_{16}H_{18}N_3SCl$). Medicinal grade methylene blue is a trihydrate, $C_{16}H_{18}N_3SCl \cdot 3H_2O$ containing 84% methylene blue and 16% water. If the above grade methylene blue is used, one drop of 1 g/L solution + 42 μg of $C_{16}H_{18}N_3SCl \cdot 3H_2O$. Therefore, one drop of 1 mg/L of S^{2-} standard solution should be theoretically equivalent to 1.8 drops of methylene blue, or one drop of this methylene blue solution I + 0.56 mg/L of sulfide. If the zinc salt of methylene blue dye $C_{16}H_{18}N_3SCl_2 \cdot ZnCl_2 \cdot H_2O$ is used, then one drop of 1 g/L solution + 40 μg of methylene blue, $C_{16}H_{18}N_3SCl$+1.9 drops of 1 mg/L S^{2-} standard, or one drop of methylene blue zinc salt + 0.53 mg/L of sulfide.

Because some amount of S^{2-} may escape out as H_2S during standard preparation and a small proportion may be oxidized to sulfate over a few hours, and also because methylene blue formation reaction may not thermodynamically go to completion, it is, therefore, always recommended that the sulfide concentration should be determined by the titrimetric iodide procedure and an average percent error of the methylene blue procedure be compared against this titrimetric procedure.

Reagents

- Aminosulfuric acid: 27 g *N,N*-dimethyl-*p*-phenylenediamine oxalate in 100 mL of 1:1 H_2SO_4 solution in a volumetric flask. Store in dark. 25 mL of this solution is diluted to 1 L with 1:1 H_2SO_4. The reagent should be stored in a dark bottle.
- Ferric chloride solution: 100 g of $FeCl_3 \cdot 6H_2O$ in 40 mL of distilled water.
- Diammonium hydrogen phosphate solution: 400 g of $(NH_4)_2HPO_4$ in 800 mL distilled water.

59 Sulfite

Sulfite, SO_3^{2-}, is a bivalent polyanion. It occurs in boiler feed water that is treated with sulfite for controlling dissolved oxygen. It also occurs in water subjected to SO_2 treatment for the purpose of dechlorination. Sulfite forms sulfurous acid, H_2SO_3, which gradually oxidizes to sulfuric acid. The excess sulfite in boiler waters can cause corrosion. Sulfite is toxic to aquatic life.

Sulfite in water may be analyzed by the following methods:

1. Ion chromatography
2. Iodometric method
3. Phenanthroline colorimetric method

Method 1 is rapid and accurate and can be applied to analyze several anions including sulfite (see Chapter 11). The minimum detection limit for sulfite by the iodometric method is 2 mg/L, while the detection limit is 0.01 mg/L for the colorimetric method.

IODOMETRIC METHOD

The sample containing sulfite is first acidified and then titrated against a standard solution of potassium iodide–potassium iodate to a blue end point, using starch indicator. The sequence of reactions is as follows.

Potassium iodate and potassium iodide react in an acid medium, liberating iodine.

$$IO_3^- + 5I^- + 6H^+ \Rightarrow 3I_2 + 3H_2O$$
$$(\text{or, } KIO_3 + 5KI + 6HCl \Rightarrow 6KCl + 3I_2 + 3H_2O)$$

The iodine produced reacts with SO_3^{2-}, oxidizing sulfite to sulfate, and is itself reduced to HI, as shown below:

$$SO_3^{2-} + I_2 + H_2O \Rightarrow SO_4^{2-} + 2HI$$

When all the sulfite in the sample is consumed, the excess iodine reacts with the starch to form a blue coloration. Thus, at the end point of the titration, when no sulfite is left, the iodine produced *in situ* from the addition of a single drop of standard iodide–iodate titrant into the acid solution forms the blue complex with starch that was previously added to the sample.

Interference

The presence of oxidizable substances in the sample would interfere in the test, thus giving high results. These include S^{2-}, $S_2O_3^{2-}$, and certain metal ions such as Fe^{2+} in the lower oxidation state. Sulfide should be removed by adding 0.5 g of zinc acetate, allowing the zinc sulfide precipitate to settle and drawing out the supernatant liquid for analysis. If thiosulfate is present, determine its concentration in an aliquot of sample by iodometric titration using iodine standard. Subtract the concentration of thiosulfate from the iodometric sulfite results to calculate the true value of SO_3^{2-}.

The presence of Cu^{2+} ion can catalyze the oxidation of SO_3^{2-} to SO_4^{2-}, which would give a low result. This is prevented by adding EDTA which complexes with Cu^{2+}. This also promotes the oxidation of Fe^{2+} to Fe^{3+}. Nitrite, which reacts with sulfite, is destroyed by adding sulfamic acid.

Procedure

Place 1 mL of HCl in an Erlenmeyer flask. Add 0.1 g of sulfamic acid. Add 100 mL of sample. Add 1 mL of starch indicator solution (or 0.1 g solid). Titrate with potassium iodide–iodate standard solution until a faint blue color develops. Run a blank using distilled water instead of the sample.

Calculation

$$\text{mg } SO_3^{2-} = \frac{(A-B)\times \text{N}\times 40{,}000}{\text{mL sample}}$$

where:

A is the mL of titrant for the sample
B is the mL of titrant for the blank
N is the normality of the KI–KIO_3 titrant

The equivalent weight of SO_3^{2-} is formula wt/2 = 80/2 or 40. The milligram equivalent, therefore, is 40,000.

Reagents

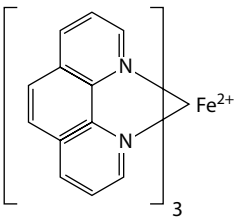
- Standard potassium iodide–iodate titrant solution, 0.0125 N: dissolve 0.4458 g of anhydrous KIO_3 (dried for several hours at 120°C) and 4.25 g of KI and 0.310 g of $NaHCO_3$ in distilled water and dilute to 1 L. The equivalent weight of KIO_3 is formula wt/6 or 35.67; thus, 0.0125 N solution is prepared by dissolving (35.7 g × 0.0125) or 0.4458 g salt in 1 L distilled water. The iodate–iodide anions upon reaction lose a total of six electrons, forming iodine. KIO_3 is the limiting reagent that determines the stoichiometry of iodine formation, while KI is used in excess as it has an additional role in starch–iodide complex formation (see Iodometric Titration).
- 1 L of titrant + 0.0125 g equivalent of SO_3^{2-} + 0.0125 × 40 g of SO_3^{2-} or 500 mg of SO_3^{2-}. Thus, 1 mL of KIO_3–KI titrant solution made of +500 μg SO_3^{2-}.
- EDTA reagent: 2.5 g of disodium EDTA in 100 mL of distilled water.

COLORIMETRIC METHOD

Sample containing sulfite on the acidification produces sulfur dioxide:

$$Na_2SO_3 + HCl \Rightarrow 2NaCl + SO_2 + H_2O$$

The liberated SO_2 is purged with nitrogen and trapped in an absorbing solution that contains Fe^{3+} and 1,10-phenanthroline. SO_2 reduces Fe^{3+} to Fe^{2+}, which reacts with 1,10-phenanthroline to produce an orange–red complex, *tris*(1,10-phenanthroline)iron(II) (also called "ferroin"), having the following structure:



The intensity of the color developed is proportional to the amount of phenanthroline complex formed, which is proportional to the concentration of sulfite in the sample. After removing the excess ferric iron with ammonium bifluoride, the absorbance is measured at 520 nm. The concentration of SO_3^{2-} in the sample is calculated from a sulfite standard calibration curve. Because SO_3^{2-} solutions are unstable, the concentration of working standard is accurately determined by potassium iodide–iodate titration before colorimetric measurement.

Certain orthophenanthrolines may be used instead of 1,10-phenanthroline. These include 5-nitro-1,10-phenanthroline, Erioglaucine A, and *p*-ethoxychrysoidine that form iron-II complexes of violet–red, yellow–green, and red colors, respectively.

Procedure

Set up an apparatus to purge out SO_2 with N_2 from an acidified sample and trap the liberated gas in an absorbing solution, as shown in Figure 59.1.

The absorbing solution consists of 5 mL of 1,10-phenanthroline, 0.5 mL of ferric ammonium sulfate, and 25 mL of distilled water taken in a 100 mL glass tube B. A few drops of octyl alcohol are added to prevent foaming.

In tube A, take 1 mL of sulfamic acid and 100 mL of sample or a sample portion diluted to 100 mL. Add 10 mL of 1:1 HCl and immediately connect tube A with tube B. Start nitrogen flow, adjust the flow between 0.5 and 1 L/min, and purge for 1 h.

Disconnect the tubes after turning off the gas. Add 1 mL of NH_4HF_2 immediately to tube B. Dilute the contents of tube B to 50 mL. Allow it to stand for 5 min. Pipet 1 mL of this solution into a 1 cm cell and read the absorbance against distilled water at 510 nm.

Repeat the above steps exactly in the same manner and read absorbance for a distilled water blank and four SO_3^{2-} standards. The stock standard should be standardized by the titrimetric method to determine the molarity of SO_3^{2-}. Prepare a calibration curve plotting absorbance versus microgram sulfite. Run at least one standard for each batch of samples.

Calculation

$$\text{mg } SO_3^{2-}/\text{L} = \frac{\mu\text{g } SO_3^{2-} \text{ from calibration curve}}{\text{mL sample}} \times 50$$

If the sample volume is the same as the volume of calibration standards taken in the analysis, a calibration curve may be plotted in ppb concentration instead of microgram mass. In such a case, read the ppb concentration of SO_3^{2-} in the sample directly from the calibration curve.

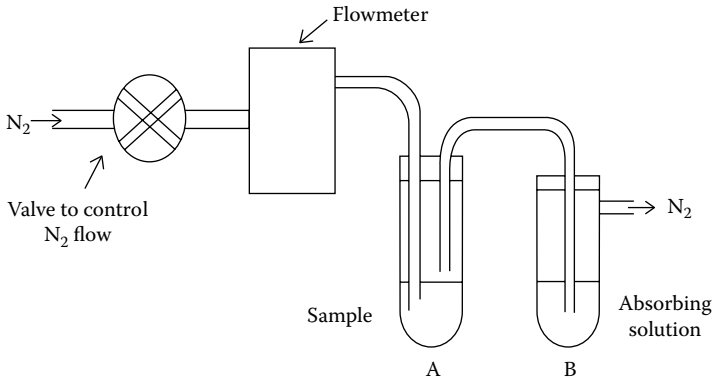


FIGURE 59.1 Diagram showing apparatus for purging out SO_2 with N_2.

TABLE 59.1
Sulfite Standards

	Dilution (mL)	Calibration Std (mg/L)	Micrograms in 1 cm Cell (1 mL Std)
1 mL stock	100	$+0.01C_s$	$+0.01C_s$
2 mL stock	100	$+0.02C_s$	$+0.02C_s$
5 mL stock	100	$+0.05C_s$	$+0.05C_s$
10 mL stock	100	$+0.10C_s$	$+0.10C_s$
20 mL stock	100	$+0.20C_s$	$+0.20C_s$

Note: C_s is the concentration of SO_3^{2-} in stock solution determined from titration.

Reagents

- Sulfite standards: dissolve 1 g of Na_2SO_3 in 1 L distilled water. Standardize this solution by titration using 0.0125 N potassium iodide–iodate titrant. (See section, Titrimetric Method in this chapter for detailed procedure.) Determine the exact concentration of this stock solution.
- Pipet 1, 2, 5, 10, and 20 mL of the stock solution into 100 mL volumetric flasks and dilute to the mark with 0.04 M potassium tetrachloromercurate, K_2HgCl_4 solution. This gives a series of sulfite standards whose concentrations are listed in Table 59.1.
- Standard potassium iodide–iodate: see section Iodometric Method.
- 1,10-Phenanthroline solution, 0.03 M: dissolve 5.95 g in 100 mL of 95% ethanol and dilute to 1 L with distilled water.
- Ferric ammonium sulfate, $NH_4Fe(SO_4)_2 \cdot 12\ H_2O$, solution, 0.01 M: add 1 mL of conc. H_2SO_4 to 1 L distilled water and dissolve 4.82 g of the salt in this acidified water. Adjust the pH of the solution between 5 and 6.
- Ammonium bifluoride, 5% solution: dissolve 5 g of NH_2HF_2 in 100 mL of distilled water. Store this reagent in a plastic bottle.
- Potassium tetrachloromercurate, 0.04 M: dissolve 10.86 of $HgCl_2$, 5.96 g of KCl, and 0.066 g of disodium EDTA in 1 L distilled water. Adjust the pH between 5.0 and 5.5. The solution is stable for 4–6 months.
- Sulfamic acid: 10 g in 100 mL of distilled water.
- Disodium EDTA, 2.5%: 2.5 g in 100 mL distilled water.

60 Surfactant
Anionic

Many anionic surfactants can react with a cationic dye such as methylene blue to form strong ion pairs that can be extracted by a suitable organic solvent and can be determined using colorimetric techniques. The anionic surfactants that respond to the methylene blue test are primarily the sulfonate ($RSO_3^- Na^+$) and the sulfate ester ($ROSO_3^- Na^+$) type substances. On the other hand, soaps and the alkali salts of fatty acids (C-10–C-20) used in certain detergents do not respond to the above test. The various anionic surfactants and their characteristic structural features are presented in Figure 60.1.

Such anionic surfactants that form ion pairs with methylene blue and that are extractable with chloroform are known as "methylene blue active substances" (MBAS). Other cationic dyes, such as crystal violet dye, may be used instead of methylene blue. Extraction of such an ion-pair complex into benzene has been reported (Hach, 1989). Detection limit = 10 μg/L.

REAGENTS

- Methylene blue reagent: 30 mg methylene blue in 500 mL water; add 41 mL of 6 N H_2SO_4 and 50 g sodium dihydrogen phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$); dilute to 1 L.
- Wash solution: 41 mL 6 N H_2SO_4 in 500 mL water; add 50 g $NaH_2PO_4 \cdot H_2O$, dilute to 1 L.
- Stock linear alkyl sulfonate (LAS) solution: Reference, LAS material may be obtained from the U.S. EPA (Environmental Monitoring Systems Laboratory, Cincinnati, Ohio). The average molecular weight of LAS should fall in the range of 310–340. LAS material in the above average molecular weight range may be specially ordered from commercial suppliers.

Stock solution is made by dissolving 100 mg of LAS in 1 L distilled water

$$1\ \text{mL} = 100\ \mu\text{g LAS}$$

A secondary standard solution is prepared from the above stock solution by diluting 1–100 mL

$$1\ \text{mL} = 1\ \mu\text{g LAS}$$

A series of calibration standard solutions are prepared from this secondary standard solution as seen in Table 60.1.

ANALYSIS

The determination of anionic surfactants in aqueous samples involves the following analytical steps:

1. Preparation of a standard calibration curve. A series of calibration standards are prepared from LAS. The concentrations of the calibration standards should range from 10 to 150 μg/L, which corresponds to a mass of 1–15 μg LAS, respectively, in 100 mL solution. Each LAS standard solution in 100 mL quantity should be treated with methylene blue reagent.

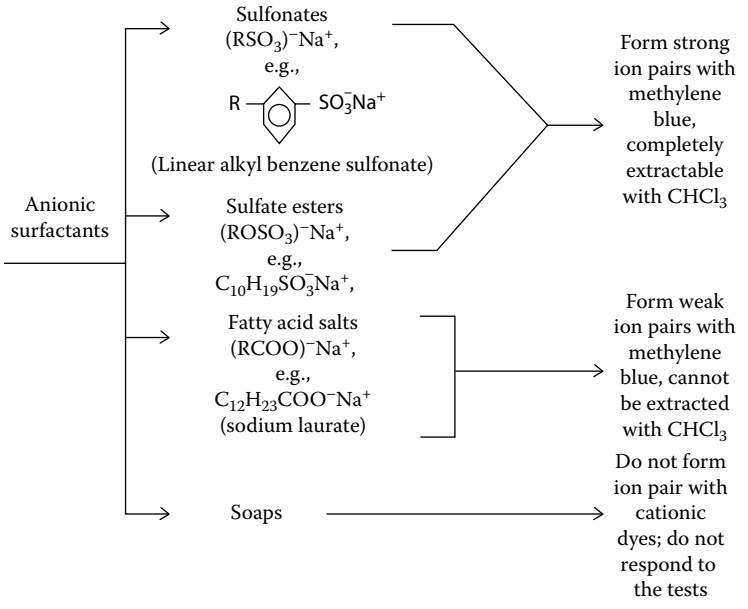


FIGURE 60.1 Schematic representation of the structural features of the various anionic surfactants.

TABLE 60.1
Series of Calibration Standard Solutions

Dilution of Secondary Standard	Concentration (μg/L)	Mass
1 mL diluted to 100 mL	10	1 μg LAS
2 mL diluted to 100 mL	20	2 μg LAS
5 mL diluted to 100 mL	50	5 μg LAS
7 mL diluted to 100 mL	70	7 μg LAS
10 mL diluted to 100 mL	100	10 μg LAS
12 mL diluted to 100 mL	120	12 μg LAS
15 mL diluted to 100 mL	150	15 μg LAS

2. The standards are taken in separatory funnels. A few drops of phenolphthalein indicator followed by 1 N NaOH solution are added dropwise until a pink color forms. This is followed by the addition of 1 N H_2SO_4 dropwise until the pink colors decolorize.
3. Add 10 mL of chloroform followed by methylene blue reagent. The separatory funnel is shaken vigorously for 30 s. Methylene blue-surfactant ion pair separates into the bottom chloroform layer. The aqueous layer should be colorless. The above chloroform extraction is performed two more times. The extracts are combined and then washed repeatedly in another separatory funnel with the acid wash solution.
4. The absorbances of the chloroform extracts of the calibration standards are read at the wavelength 652 nm against a chloroform blank. A calibration curve is constructed by plotting absorbance against microgram LAS.

Sample Analysis

A 100 mL sample aliquot is extracted as above with chloroform. The absorbance of the chloroform solution is read at 652 nm and the amount of anionic surfactants active to methylene blue is determined from the standard calibration curve.

Calculation

$$\text{mg MBAS/L} = \frac{A}{\text{mL sample}}$$

where A is μg LAS read from the calibration curve.

The highly concentrated sample must be diluted such that the MBAS concentration falls within the linear calibration range. Such concentrations, however, in routine environmental analyses are rarely encountered.

INTERFERENCE

The presence of chloride, nitrate, sulfide, organic sulfonates, cyanates, organic amines, and particulate matters may interfere in the test. The two major interferences, chloride and nitrate, however, may be removed in the acid backwash steps. Sulfide reacts with methylene blue to form a colorless complex. Interference from sulfide may be removed by treating the sample with a few drops of 30% H_2O_2, whereupon sulfide is converted into sulfate.

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61 Thiocyanate

Thiocyanate is a monovalent polyanion that has the formula SCN^-. This anion is rarely found in wastewater. However, cyanide-containing waste or water on contact with sulfides can form thiocyanates. On chlorination, the thiocyanate could react with chlorine to form highly toxic cyanogen chloride, CNCl. Thiocyanate in water may be analyzed using (1) colorimetric method and (2) spot test. The latter method is a rapid spot test that can give semiquantitative results. Preserve samples at pH below 2 and refrigerate.

COLORIMETRIC METHOD

Thiocyanate reacts with ferric ion under acidic conditions to form ferric thiocyanate, which has an intense red color.

$$SCN^- + Fe^{3+} \rightarrow Fe(SCN)_3$$

The intensity of color of the ferric thiocyanate formed is proportional to the concentration of thiocyanate ion in the sample. The absorbance or transmittance is measured at 460 nm using a spectrophotometer or a filter photometer. The concentration of SCN^- in the sample is determined from a standard calibration curve. The detection range of this method is 0.1–2.0 mg SCN^-/L. Dilute the samples if the concentration exceeds this range.

Interference

Reducing substances, hexavalent chromium and colored matter, interfere with the test. Reducing substances that may reduce Fe^{3+} to Fe^{2+} and thus prevent the formation of thiocyanate complex may be destroyed by adding a few drops of H_2O_2. Add $FeSO_4$ to convert Cr^{6+} to Cr^{3+} at a pH below 2. Cr^{3+} and Fe^{3+} so formed are precipitated out when the pH is raised to 9 with NaOH.

Sample pretreatment is necessary if the sample contains color and various organic compounds. To remove such interference, pass the sample through a purified, solvent-washed adsorbent resin bed.

Procedure

To 100 mL of sample or pretreated sample eluant eluted through the adsorbent resin, add a few drops of HNO_3 to bring down the pH to 2. Add 5 mL ferric nitrate solution and mix. Fill a 5 cm cell and measure absorbance against a reagent blank at 460 nm.

Prepare a calibration curve by plotting either mg SCN^- or mg/L SCN^- versus absorbance using the standard solutions (see below). Determine the concentration of thiocyanate in the sample from the standard curve.

Calculation

$$\text{mg } SCN^-/L = \frac{\text{mg } SCN^- \text{ read from the calibration curve} \times 1000}{\text{mL sample}}$$

If the sample volume is the same as the volumes of working standards, and if the calibration curve is plotted in mg/L concentration unit, then the concentration of thiocyanate as mg SCN^-/L can be directly read from the calibration curve. Multiply the result by the dilution factor if the sample was diluted.

Reagents and Calibration Standards

- Ferric nitrate, $Fe(NO_3)_3 \cdot 9H_2O$ solution. 1 M: dissolve 404 g in 800 mL of distilled water, add 80 mL of conc. HNO_3 and dilute to 1 L.
- Thiocyanate standard solutions: 1.673 g potassium thiocyanate, KSCN in distilled water, diluted to 1 L. This stock solution = 1000 mg SCN^-/L or 1 mL = 1 mg SCN^-. Prepare a secondary standard from the stock solution by diluting 1 mL stock solution to 100 mL with distilled water. Secondary standard = 10 mg SCN^-/L or 1 mL = 0.01 mg SCN^-. Prepare a series of calibration standards by diluting the secondary standard with distilled water as follows:

Secondary Std (mL)	Diluted to (mL)	SCN^- Mass (mg)	SCN^- Conc. (mg/L)
1	100	0.01	0.1 (0.1 ppm)
2	100	0.02	0.2 (0.2 ppm)
5	100	0.05	0.5 (0.5 ppm)
10	100	0.10	1.0 (1 ppm)
20	100	0.20	2.0 (2 ppm)

SPOT TEST FOR THIOCYANATE

Thiocyanate reacts with chloramine-T on heating at pH below 8 to form cyanogen chloride, CNCl. The latter forms red color after adding pyridine–barbituric acid reagent. This test is similar to that of cyanide. Therefore, prior to chloramine treatment, the sample is treated with formaldehyde to mask the effect of cyanide. The addition of four drops of 37% formaldehyde solution should mask up to 5–10 mg CN^-/L if present in the sample.

Reagents are added after pretreatment of the sample. The spot test is performed in a porcelain spot plate with 6–12 cavities. The test is performed using a few drops of sample, standards, and reagents. The color developed is compared with thiocyanate standards. The test is semiquantitative and is suitable for screening SCN^- in water.

Procedure

Heat 25 mL of sample in a water bath at 50°C. Add four drops of formaldehyde solution (37% pharmaceutical grade). Continue heating for another 10 min. The formaldehyde treatment would mask the effect of cyanide if present in the sample.

If the pH of the solution is above 10, add about 0.2 g Na_2CO_3 and mix. Add a drop of phenolphthalein indicator that will turn the solution red (or pink) in the alkaline medium. Add 1 N HCl dropwise until the color disappears. Place three drops of the above pretreated sample, three drops of distilled water, and three drops each of thiocyanate standards (0.05, 0.1, and 0.2 mg SCN^-/L) in the cavities of a porcelain spot plate. Add one drop of chloramine-T solution to each cavity and mix with a clean glass rod. This is followed by the addition of one drop of pyridine–barbituric acid to each cavity. Again, mix the contents and allow it to stand for a minute. If thiocyanate is present, the sample spot will turn pink to red, depending on the concentration of SCN^- in the sample. If deep red coloration is produced, dilute the sample and repeat the test.

The above test would give SCN^- concentration in an estimated range. For greater accuracy, place more standards in the cavities of a spot plate for color comparison. Alternatively, once the SCN^- concentration range in the sample is known from the above screening test, prepare several thiocyanate standards within that range and repeat the spot test for color comparison.

Reagents

- Chloramine-T solution: 1 g powder in 100 mL distilled water.
- Pyridine–Barbituric acid: see Chapter 19.
- Thiocyanate standard solution: the stock standard is made from KSCN. The secondary and working standards are prepared from this. See section Colorimetric Method.

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62 Total Dissolved Solids and Specific Conductance

Theoretical Calculations

TOTAL DISSOLVED SOLIDS

The total dissolved solids (TDS) in aqueous samples are determined by filtering an aliquot of the sample, evaporating the filtrate to dryness in a weighted dish, and then measuring the weight of the dried residue to a constant weight. The residue is dried at 180°C at least for an hour.

TDS is essentially attributed to many soluble inorganic salts that are commonly found in surface water and groundwater. The ions that are often found in significant concentrations, contributing to the TDS include the metal ions (e.g., Na^+, K^+, Mg^{2+}, and Ca^{2+}) and anions (e.g., Cl^-, F^-, SO_4^{2-}, CO_3^{2-}, NO_3^{2-}, and SiO_3^{2-}). In addition, certain metal ions, such as Al^{3+}, Cr^{3+}, Fe^{3+}, and Mn^{2+} also often occur in many waters. The latter, however, occur as insoluble oxides and hydroxides and, therefore, do not contribute to TDS at the ambient temperature and the pH conditions.

Total dissolved solids may be calculated as follows by summing up the concentrations of the common soluble ions found in the water:

$$\text{TDS, mg/L} = [Na^+ + K^+ + Ca^{2+} + Mg^{2+} + Cl^- + SO_4^{2-} + NO_3^- + SiO_3^{2-} + F^- + 0.6\,(\text{alkalinity, as } CaCO_3)]\ \text{mg/L}$$

In the above calculation, alkalinity (as $CaCO_3$) is multiplied by the factor 0.6 to account for the concentrations of CO_3^{2-}, HCO_3^-, and OH^-. Carbonate constitutes 60% of $CaCO_3$ (MW 100). Since there might be other soluble ions present in the sample as well, the TDS, calculated as above cannot be greater than the measured TDS. In other words, the measured TDS should be either equal or slightly greater than the calculated TDS.

CONDUCTIVITY

Specific conductance, or the conductivity of a solution, is attributed to the ionic species (cations and anions) present in the solution. The conductivity to TDS ratio should be between 1.4 and 1.8, that is,

$$\frac{\text{Conductivity (expressed as } \mu\text{mhos/cm)}}{\text{TDS (mg/L)}} = 1.4 - 1.8$$

or

$$\frac{\text{TDS}}{\text{Conductivity}} = 0.55 - 0.70$$

The conductivity of a solution may be accurately determined by a conductivity meter. If the sample resistance of the sample is measured, conductivity at 25°C is calculated as follows:

$$k = \frac{(1{,}000{,}000)(C)}{R[1 + 0.019(t - 25)]}$$

where:

k is the conductivity (μmhos/cm)
C is the cell constant (cm^{-1})
R is the resistance of the sample in ohm, as measured
t is the temperature of the sample
C is determined using a 0.01 M KCl solution

$$C(cm^{-1}) = (0.001412)(R_{KCl})[1 + 0.019(t - 25)]$$

where R_{KCl} is resistance, in ohms of 0.01 M KCl solution.

The units for k are as follows.

Conductivity of a solution is usually expressed as μmhos/cm. The SI units for conductivity and their conversion are as follows:

$$1\,\mu\text{mhos/cm} = 1\,\mu\text{S/cm (microsiemens/centimeter)}$$
$$= 0.1\text{ mS/m (millisiemens/meter)}$$

or

$$1\text{ mS/m} = 10\,\mu\text{mhos/cm}$$

where

$$1\text{ S (siemens)} = \frac{1}{\text{ohm}}$$

Conductivity of a solution (a standard solution) may be estimated using the following equation:

$$k = \frac{\lambda c}{0.001}$$

where:

k is the conductivity (μmhos/cm)
λ is the equivalent conductivity (mho-cm^2/equivalent)
c is the gram equivalent/L

Such calculation, however, does not give an accurate determination of k. It applies to a solution of infinity dilution and, therefore, is susceptible to an appreciable departure from the true value at higher concentrations. This is illustrated in the following example.

EXAMPLE 62.1

Calculate the conductivity of 0.01 M KCl solution using the above equation.

$$KCl_{(aq)} \rightarrow K^+_{(aq)} + Cl^-_{(aq)}$$

Thus, 0.01 M KCl solution is 0.01 M K^+ and 0.01 M Cl^- which is also 0.01 equivalent/L for both K^+ and Cl^-.

$$\text{Thus, } k \text{ due to } K^+ = \frac{\lambda c}{0.001} = \frac{73.5 \times 0.01}{0.001} = 735$$
$$\text{and } k \text{ due to } Cl^- = \frac{\lambda c}{0.001} = \frac{76.4 \times 0.01}{0.001} = 764$$

The λ values for K^+ and Cl^- at the infinite dilution are 73.5 and 76.4 mho-cm^2/equivalent, respectively (Table 62.1). Therefore, the conductivity of 0.01 M (or 0.01 N) KCl solution is estimated to be 735 + 764 or 1499 μmhos/cm, which is a distinct deviation from the measured value of 1412 μmhos/cm. This problem may be overcome by using the ion activity coefficient as shown below in the following equations and examples.

The conductivity of a sample may be theoretically calculated if the concentrations of the ions present in the sample are known. Such calculations may be performed, using a series of equations, as follows:

$$k_{calc} = k^\circ \times y^2$$

where:
k_{calc} is the conductivity calculated
k° is the conductivity at infinity dilution
y is the monovalent ion activity coefficient

y can be determined at the ambient temperature (ranging between 20°C and 30°C) for any solution that is less than 0.5 M in concentration, using the Davies equation as follows:

$$y = 10^{-0.5[\{(a)^{0.5} \div (1+(a)^{0.5})\} - 0.3 \times a]}$$

where a is the ionic strength in molar units; a can be calculated from the following equation:

$$a = \frac{\sum z^2 c}{2000}$$

where:
z is the charge on the ion
c is the concentration of the ion, expressed as millimole (mM)

Finally, k° is calculated from the following equation:

$$k^\circ = z \times \lambda^\circ \times c$$

where λ° is the equivalent conductance, expressed as mho/cm^2.

The value of λ° for ions in water at 25°C has been measured. The λ° values for some common ions are shown in Table 62.1.

The theoretical determination of conductivity is illustrated in the following two examples.

EXAMPLE 62.2

Calculate the conductivity of 0.01 M KCl solution at 25°C.

KCl is a strong electrolyte that readily dissociates into K^+ and Cl^- ions when dissolved in water

$$KCl_{(aq)} \rightarrow K^+_{(aq)} + Cl^-_{(aq)}$$

TABLE 62.1
Equivalent Conductance, λ° for Common Ions in Water at 25°C

Ions	Equivalent Conductance λ° (mho-cm^2/Equivalent)
H^+	350.0
NH_4^+	73.5
1/3 Al^{3+}	61.0
Na^+	50.1
K^+	73.5
1/2 Ca^{2+}	59.5
1/2 Mg^{2+}	53.1
1/2Mn^{2+}	53.5
1/2 Fe^{2+}	54.0
1/3 Fe^{3+}	68.0
1/2 Ni^{2+}	50.0
1/2Cu^{2+}	53.6
1/2 Pb^{2+}	71.0
Ag^+	61.9
OH^-	198.6
F^-	54.4
HCO_3^-	44.5
1/2CO_3^{2-}	72.0
1/2SO_4^{2-}	80.0
Ac^{-}[a]	40.9
Cl^-	76.4
NO_3^-	71.4
NO_2^-	71.8
$H_2PO_4^-$	33.0
1/2HPO_4^{2-}	57.0
Br^-	78.1
I^-	76.8
ClO_2^-	52.0
ClO_3^-	64.6
ClO_4^-	67.3
HS^-	65.0
HSO_3^-	50.0
HSO_4^-	50.0
CN^-	78.0
CNO^-	64.6
OCN^-	64.6
SCN^-	54.9
MnO_4^-	61.3
1/2CrO_4^{2-}	85.0

[a] Acetate ion (CH_3COO^-).

As we know, the conductivity, $K_{calc} = k^\circ \times y^2$. Now, we have to determine k° and y.

$$K^\circ = z\lambda^\circ c$$

Both K^+ and Cl^- are monovalent ions, having a charge of +1 and −1, respectively. Thus, the magnitude of z for each ion is 1 unit. The equivalent conductance's, λ° for K^+ and Cl^- from Table 62.1 are 73.5 and 76.4 mho-cm^2/equivalent, respectively. The millimolar (mM) concentration of each of these ions is (0.01 M × (1000 mM/1 M)) or 10 mM.

Now k° for KCl = k° for K^+ + k° for Cl^-.

Thus, the k° for $K^+ = 1 \times 73.5 \times 10 = 735$ and $Cl^- = 1 \times 76.4 \times 10 = 764$. Therefore, the k° for KCl = 735 + 764 = 1499.

Now, we have to calculate the value for y.

$$y = 10^{-0.5[(a)^{0.5}+(1+(a)^{0.5})-0.3a]}$$

The ionic strength,

$$a = \frac{\sum z^2 c}{2000}\text{M} \quad \text{or} \quad \frac{z^2c \text{ for } K^+ z^2c \text{ for } Cl^-}{2000}$$

and c = 10 mM for both the K^+ and Cl^-, respectively.

Therefore,

$$a = \frac{1^2 \times 10 \text{ (for } K^+) + 1^2 \times 10 \text{(for } Cl^-)\text{ M}}{2000} = \frac{20}{2000} \text{ or } 0.001\,\text{M}$$

Therefore, $y = 10^{-0.5\left[\left\{0.001^{0.5} \div \left(1+0.001^{0.5}\right)\right\} - 0.3\times 0.001\right]}$

$$10^{-0.0138} = 0.9687$$

Substituting the values for y and k°, we can determine the theoretical conductivity as

$$k_{calc} = 1499 \times (0.9687)^2 \text{ or } 1407\ \mu\text{mhos/cm}$$

This closely agrees with the experimental value of 1412 μmhos/cm.

EXAMPLE 62.3

Analysis of an aqueous sample showed the following results: Cl^- 207 mg/L, SO_4^{2-} 560 mg/L, NO_3^- 22.5 mg/L, Na^+ 415 mg/L, and Ca^{2+} 54 mg/L. The pH of the sample was found to 3.8. Calculate the conductivity of the sample.

At first, we convert the mg/L concentration of these ions into their mmole concentrations.

$$Cl^- = \left|\frac{207\text{ mg}}{1\text{L}} \times \frac{1\text{mmol}}{35.45\text{ mg}} \times \frac{1\text{L}}{1\text{mmol}}\right| = 5.48\text{ mM}$$

$$SO_4^{2-} = \left|\frac{560\text{ mg}}{1\text{L}} \times \frac{1\text{mmol}}{96\text{ mg}} \times \frac{1\text{L}}{1\text{mmol}}\right| = 5.83\text{ mM}$$

$$NO_3^- = \left|\frac{22.5\text{ mg}}{1\text{L}} \times \frac{1\text{mmol}}{62\text{ mg}} \times \frac{1\text{L}}{1\text{mmol}} = 0.363\text{ mM}\right.$$

$$Na^+ = \left|\frac{415\text{ mg}}{1\text{L}} \times \frac{1\text{mmol}}{23\text{ mg}} \times \frac{1\text{L}}{1\text{mmol}} = 18.04\text{ mM}\right.$$

$$Ca^{2+} = \left|\frac{54\text{ mg}}{1\text{L}} \times \frac{1\text{mmol}}{40\text{ mg}} \times \frac{1\text{L}}{1\text{mmol}} = 1.35\text{ mM}\right.$$

$$\text{pH} = \left|3.8;\ C_{H^+} = 10^{-\text{pH}} = 10^{-3.8}\right.$$

$$= 0.00158\text{ M}$$

$$H^+ = 0.158\text{ mM}$$

Now we calculate $k°$ for each of these ions, using the formula

$$k° = z \times \lambda° \times c\ (\lambda° \text{ values are presented in Table 62.1})$$

$$k° \text{ for } Cl^- = 1 \times 76.4 \times 5.84 = 446.2$$

$$k° \text{ for } SO_4^{2-} = 2 \times 80.0 \times 5.83 = 932.8$$

$$k° \text{ for } NO_3^- = 1 \times 71.4 \times 0.363 = 25.9$$

$$k° \text{ for } Na^+ = 1 \times 50.1 \times 18.04 = 903.8$$

$$k° \text{ for } Ca^{2+} = 2 \times 59.5 \times 1.35 = 160.6$$

$$k° \text{ for } H^+ = 1 \times 350.1 \times 0.158 = 55.3$$

$$k° = 446.2 + 932.8 + 25.9 + 903.8 + 160.6 + 55.3$$

$$= 2524.6$$

Next, we calculate the ionic strength, a, for the sample using the equation

$$a = \frac{\sum z^2 C}{2000}$$

$$= \frac{(1 \times 5.84) + (4 \times 5.83) + (1 \times 0.363) + (1 \times 18.04) + (4 \times 1.35) + (1 \times 0.158)}{2000}$$

$$= 0.02656\text{ M}$$

From the value of a, we now calculate y, the monovalent ion activity, from the equation

$$y = 10^{-0.5[\{(a)^{0.5} \div (1+(a)^{0.5})\} - 0.3a]}$$

$$= 10^{-0.06607}$$

$$= 0.8589$$

Therefore, $k_{calc} = 2524.6 \times (0.8580)^2 = 1862$ μmhos/cm.

Thus, the conductivity of any aqueous sample may be precisely calculated, as seen in Examples 62.2 and 62.3, if we know the concentrations of the metal ions and the anions in the sample. The presence of such metal ions and the anions and their concentrations may be simultaneously measured by an ICP atomic emission spectrophotometer and an ion chromatograph, respectively.

63 Volatile Organic Compounds

A number of organic substances that are found in the environmental matrices or released into the environment from various industrial processes are referred to as "volatile compounds" for their relatively low boiling points and high vapor pressures. There are however no definitive criteria to define the boiling point or the vapor pressure range of such substances. The term "volatile" compounds includes a wide range of substances that may be gases at ordinary temperatures, such as methyl chloride or liquids like carbon tetrachloride with a boiling point greater than that of water. Under this general term, we may include any substance that can be purged out of water under a flow of a purging gas, or likewise thermally desorbed out from the sample matrices when heated under a carrier gas. The term "volatile organic compounds" in general applies to the sample extraction technique. Several methods may be found in the literature for analyzing such volatile organic compounds in aqueous and nonaqueous matrices (APHA, AWWA, and WEF, 2005; NIOSH, 1994; Patnaik, 2004; U.S. EPA, 1986, 1992, 1999). Such extraction techniques may vary with the sample matrices. Compounds are mostly detected by GC using a suitable GC detector or by a mass spectrometer.

WATER ANALYSIS

The volatile compounds are removed from the aqueous samples by what is known as the "purge and trap" method. Measured volumes of an aqueous sample are placed in a purging and trap apparatus and subjected to a flow of helium gas for a certain length of time. The compounds purged out of water and transferred into the vapor phase then pass onto an adsorbent trap packed with a mixture of adsorbents, such as activated charcoal, tenax, and silica gel. The volatile analytes in the sample are now adsorbed in the trap. The trap is then heated at a high temperature under the flow of the purging or carrier gas to desorb out the compounds bound to the adsorbents in the trap. The desorbed analytes are transferred into a GC inlet port. The compounds are separated on the GC column and detected by a GC detector or a mass spectrometer interfaced to the GC. The purge and trap method is not only an extraction technique to separate the volatile analytes from water but also is a technique to concentrate those analytes on the adsorbent traps. Thus, the detection limits for the compounds can be lowered by using larger volumes of samples. It may be noted here that the adsorbent materials used in the traps should be in sufficient amounts so that any analyte at excessively high level in the sample does not overload the trap. In addition, the temperatures to which the adsorbent materials are to be heated and the time of heating should be sufficiently high to desorb out all the analytes from the traps, as well as ensure that the efficiency of the adsorbents is regenerated for repeat use. In addition, the temperatures must not be excessively high to decompose the compounds. Similarly, the flow rate of the purging gas is equally important. Under a high flow of the purging gas, the compounds purged out of waters may not have sufficient contact time with the adsorbents for their adsorption. On the other hand, a slow flow rate will delay the time of analysis. In addition, an added advantage of such purge and trap technique is that no further sample cleanup steps are required here, unlike that needed for most other types of organic analytes extracted by the traditional LLEs. On the other hand, a major disadvantage of this method is that water-soluble analytes such as acetone or ethanol cannot be fully separated out from their aqueous matrix.

The conditions under which the analytes are separated out from their aqueous matrices, adsorbed over the traps, and desorbed out must be optimized to obtain the best performance of the method. A typical set of conditions under which such purging and trapping of volatile organics from the

environmental waters are carried out is outlined below for a general guidance (APHA, AWWA, and WEF, 2005). Any equivalent or modified conditions may be used to suit the need.

Apparatus

The purge and trap system consists of a purging device, an adsorbent trap, and a desorber. The purging device consists of a series of glass tubes to hold several samples. Each sample tube is attached to a sample inlet, two-way syringe valve, syringe needle passing through a rubber septum, and a glass frit of medium porosity at the bottom. Needle spargers may be used instead of the glass frit. The purge gas should be introduced at the base of the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purging devices are generally designed to hold 25 mL of samples with a water column of at least 5 cm deep. The gaseous headspace between the water column and the trap should be less than 15 mL. Such purge and trap apparatus are commercially available. Smaller devices to accept 5 mL samples are also commercially available. Larger volume of samples, usually, 25 mL should be preferred over smaller volumes to attain lower detection levels. A 25 mL or a 5 mL syringe should be used to introduce the samples into the purging device. Helium or nitrogen may be used as the purge gas at a flow rate of 40 mL/min for a total purging time of 11 min.

The trap is usually a 25 cm long tube with an inside diameter of 3 mm. It is wrapped with resistance wire for electrical heating, attached to an electronic temperature control and a pyrometer, and a controller sensor or thermocouple. The trap is packed with different adsorbents and glass wool is placed at both its ends. A typical packing composition contains one-third heights of 2,6-diphenyl oxide polymer (Tenax), silica gel, and coconut charcoal, respectively. Use of methyl silicone coating, such as 3 OV-1 and silanized glass wool is recommended to protect the adsorbents. The trap should be conditioned overnight as per the manufacturer's instructions before initial use and also conditioned daily accordingly for a shorter time, as required. The analytes are desorbed out by heating the trap at 180°C for 4 min while back flushing with the inert gas. The trap is baked at this temperature for 5–7 min after each analysis and cooled to ambient temperature for the next analysis.

The compounds thermally desorbed out from the trap are then carried over with the inert gas onto the capillary GC column for their separation and subsequent analysis. The GC is interfaced to one or more detectors, such as an FID, ECD, PID, or to a mass spectrometer for the identification and quantitation of the compounds. If unknown compounds present in the samples are to be identified, then a mass spectrometer must be used. Otherwise, to determine the target compounds traditional GC detectors should serve the purpose. The selection of GC columns, their lengths and film thickness, resolution efficiency, and the detectors is discussed in Chapter 3.

GC and MS Conditions

The GC and the MS conditions for the analyses of volatile organics must meet certain QC requirements. The following set of conditions is presented below to serve as simple guidelines. Alternate columns and conditions, however, may be used if the precision and accuracy of the analysis are met and the separations of the compounds and their detection limits are satisfactorily achieved.

GC conditions: Column: 60 m long, 0.75 mm ID, 1.5 μm film thickness, VOCOL (Supelco Inc.) wide-bore capillary column or 30 m long, 0.53 mm ID, 3-μm film thickness, DB-624 (J&W Scientific) mega-bore capillary column or 30 m long, 0.32 mm ID, 1 μm film thickness, DB-5 (J&W Scientific) capillary column or equivalent; Temperature, 35°C for 4 min, 4°C/min to 50°C, 10°C/min to 175°C, 4 min; injector 250°C; detector 300°C; GC detectors, electrolytic conductivity detector, PID or a mass selective detector (mass spectrometry).

MS conditions and performance criteria: electron energy 70 eV (nominal); mass range 35–300; scan time, at least five scans per peak but not more than 2 s/scan; tuning substance, 4-BFB (25 ng), base peak at mass 95 (100% relative abundance), the *m/z* abundance criteria for all other masses of BFB must be within the acceptance range (as specified in Chapter 4).

Quantitation. The quantitation of the volatile organic compounds in samples may be performed either by the internal standard method or by the external standard method (discussed in Chapter 3). The calibration standard solutions of all such volatile organic compounds may be prepared from their stock standard solutions that can be purchased commercially. If using a GC/MS the compounds detected in the samples must be quantified from the abundances of their primary ions against that in their calibration standard solutions. In addition, in the GC/MS analysis, if some target compounds are to be quantified it is recommended to run the samples in the SIM mode to achieve lower detection limits over that of in the SCAN mode, However, lower detection limits can be achieved using an electrolytic conductivity detector or a PID. The detection limits for some common volatile compounds by the purge and trap method using 25 mL sample and either one of the above GC detectors may range between 0.02 and 0.06 μg/L. In comparison, the detection limits of such analytes by GC/MS fall in the range 0.03–0.2 μg/L. The internal standard and the surrogate standard in the analysis are fluorobenzene and 1,2-dichlorobenzene-d_4, respectively. Alternate compounds may be used if they do not interfere or react with the analytes and satisfy the method criteria.

SOIL, SEDIMENTS, AND SOLID WASTE

U.S. EPA's SW Methods

The analytical techniques to measure the volatile organic compounds in solid matrices are more or less the same as that for the aqueous samples discussed above. Some differences, however, may be noted in the sample preparation techniques. U.S. EPA's SW-846 methods describe detailed procedures that can be applied not only to the solid matrices but also to the aqueous wastes and sludge, waste oils, and groundwater. There are two such SW-846 methods, namely, Method 8261 and Method 8260B, both based on GC/MS for analyzing volatile organic compounds in a variety of solid waste matrices. Method 8260 may be applied to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludge, caustic liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soil, and sediments. Method 8261 may also be applied to measure volatile organics in all types of matrices including animal tissues and also to determine some low boiling semivolatile compounds. These methods are used to analyze the volatile organic compounds regulated under the RCRA of the U.S. Environmental Protection Agency. These methods are briefly outlined below.

Method 8260 lists a total of 108 compounds including eight compounds that are surrogates and internal standards. The names of these compounds along with their CAS Registry Numbers are presented in Table 63.1. These substances have boiling points below 200°C. Many volatile water-soluble compounds may also be analyzed by this method by the use of azeotropic distillation or closed-system vacuum distillation. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, aldehydes, ketones, ethers, acetates, acrylates, nitriles, and sulfides. In addition, certain compounds that have relatively higher boiling points and higher molecular weights can also be determined by this method. There are additional 21 compounds of such types mentioned in this method. In this method, the volatile compounds are usually introduced into the gas chromatograph by the purge and trap technique. The compounds, however, can be extracted from the sample matrices by other techniques too based on their water solubility, polarity, and boiling points. The sample introduction method should always be considered as an important step in such analysis because it can determine the recovery of compounds and their detection limits. Various sample preparation methods are discussed below and summarized in Table 63.2. The compounds are directly introduced into a wide-bore capillary column of 0.53 mm thickness. They may alternatively be cryofocused on a capillary precolumn from which they are flash evaporated to a narrow-bore capillary column of 0.25 or 0.32 mm film thickness. Wide-bore columns normally require a jet separator whereas narrow-bore columns are directly interfaced to the ion source.

TABLE 63.1
Purgeable Organic Compounds

Compounds	CAS Registry Number	Mass Ions
Benzene*	71-43-2	78, 51, 52, 77, 39
Bromobenzene*	108-86-1	77, 156, 158, 51
Bromochloromethane	74-97-5	49, 128, 130, 93
Bromodichloromethane	75-27-4	83, 85, 47, 129
Bromoform	75-25-2	173, 171, 175, 91, 81
Bromomethane	74-83-9	94, 96, 79, 81
n-Butylbenzene*	104-51-8	91, 92, 134, 65
sec-Butylbenzene*	135-98-8	105, 134, 91, 77
tert-Butylbenzene*	98-06-6	119, 91, 134, 41
Carbon tetrachloride	56-23-5	117, 119, 121, 82, 47
Chlorobenzene*	108-90-7	112, 77, 51, 114
Chloroethane	75-00-3	64, 28, 29, 27, 49, 66
Chloroform	67-66-3	83, 85, 47
Chloromethane	74-87-3	50, 15, 52
2-Chlorotoluene*	95-49-8	91, 126, 63, 39
4-Chlorotoluene*	106-43-4	91, 126, 39, 63
Dibromochloromethane	124-48-1	127, 129, 48, 91, 208
1,2-Dibromo-3-chloropropane	96-12-8	57, 157, 75, 28
1,2-Dibromoethane	106-93-4	27, 107, 109
Dibromomethane	74-95-3	174, 93, 95, 172, 176
1,2-Dichlorobenzene*	95-50-1	146, 148, 111, 75
1,3-Dichlorobenzene*	541-73-1	146, 148, 111, 75
1,4-Dichlorobenzene*	106-46-7	146, 148, 111, 75
Dichlorodifluoromethane	75-71-8	85, 87, 50
1,1-Dichloroethane	75-34-3	63, 27, 65, 98
1,2-Dichloroethane	107-06-2	62, 27, 49, 98
1,1-Dichloroethene*	75-35-4	61, 96, 98, 63
cis-1,2-Dichloroethene*	156-59-2	61, 96, 98, 63
trans-1,2-Dichloroethene*	156-60-5	61, 96, 98, 63
1,2-Dichloropropane	78-87-5	63, 61, 27, 41, 76
1,3-Dichloropropane	142-28-9	76, 41, 27, 78, 49
2,2-Dichloropropane	594-20-7	77, 41, 97, 61
1,1-Dichloropropene*	563-58-6	75, 39, 110, 112
cis-1,3-Dichloropropene*	10061-01-5	75, 39, 110, 112
trans-1,3-Dichloropropene*	10061-02-6	75, 39, 110, 112
Ethylbenzene*	100-41-4	91, 106, 51, 78
Hexachlorobutadiene*	87-68-3	225, 190, 118, 260
Isopropylbenzene*	98-82-8	105, 120, 51, 77
p-Isopropyltoluene*	99-87-6	119, 134, 91, 39
Methyl-*t*-butyl ether*	1634-04-4	73, 57, 41, 43, 29
Methylene chloride	75-09-2	49, 84, 86, 51
Naphthalene*	91-20-3	128, 102, 51, 64
n-Propylbenzene*	103-65-1	91, 120, 65
Styrene*	100-42-5	104, 78, 51, 102
1,1,1,2-Tetrachloroethane	630-20-6	131, 133, 117, 119, 95
1,1,2,2-Tetrachloroethane	79-34-5	83, 85, 168
Tetrachloroethene*	127-18-4	166, 164, 131, 94

(*Continued*)

TABLE 63.1 (*Continued*)
Purgeable Organic Compounds

Compounds	CAS Registry Number	Mass Ions
Toluene*	108-88-3	91, 93, 39, 65
1,2,3-Trichlorobenzene*	87-61-6	180, 182, 145, 109
1,2,4-Trichlorobenzene*	120-82-1	180, 182, 145, 109
1,1,1-Trichloroethane	71-55-6	97, 99, 61, 117
1,1,2-Trichloroethane	79-00-5	97, 83, 61, 132, 99
Trichloroethene*	79-01-6	130, 95, 132, 60, 97
Trichlorofluoromethane	75-69-4	101, 103, 66, 35
1,2,3-Trichloropropane	96-18-4	75, 110, 39, 49
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	101, 151, 103, 85
1,2,4-Trimethylbenzene*	95-63-6	105, 120, 118, 77
1,3,5-Trimethylbenzene*	108-67-8	105, 120, 118, 77
Vinyl chloride*	75-01-4	62, 27, 64
o-Xylene*	95-47-6	91, 106, 51, 77
m-Xylene*	108-38-3	91, 106, 51, 77
p-Xylene*	106-42-3	91, 106, 51, 77

Note: The aromatic and olefinic compounds marked with asterisks (*) can also be analyzed by GC-PID.

U.S. EPA Methods 5030 and 5035 involve purge and trap analyses, and are similar to that discussed above under water analyses. Method 5035, however, uses a closed system purge and trap device that provides more accurate data because the loss of volatiles is minimized. In addition, this method includes a technique for the extraction of oily waste using methanol. Method 5031 is an azeotropic distillation technique to analyze certain types of nonpurgeable water-soluble volatile organics. The sample is distilled in an azeotropic distillation apparatus usually for 1 h and the aqueous distillate is directly injected into a GC or a GC/MS system. Method 5032 is a closed-system vacuum distillation technique for the analysis of many volatile and nonvolatile water-soluble organics in aqueous samples, solids, and oily wastes. The sample is introduced into a flask attached into

TABLE 63.2
Sample Preparation/Extraction Methods[a] for VOCs

Method	Sample Matrix	Preparation/Extraction Technique
3585	Oily waste	Solvent dilution
5021	Solids	Automated headspace
5030	Aqueous	Purge and trap
5031[b]	Aqueous	Azeotropic distillation
5032[c]	Aqueous and solids	Vacuum distillation
5035	Solids, oily wastes, solvents	Closed system purge and trap
5041[d]	Air sampled by VOST[e]	Purge-and-trap from VOST

[a] The above methods are cited from U.S. EPA's Solid Wastes 846 Methods.
[b] Polar volatile organic compounds are measured by this method.
[c] This method is applicable for both nonpolar and polar volatile organics.
[d] This method measures the principal organic hazardous constituents in air.
[e] VOST, volatile organic sampling train.

a vacuum distillation apparatus. Water is removed under vacuum at a pressure of 10 Torr, the vapor pressure of water. The water vapor is passed over a condenser coil chilled to a temperature below −10°C resulting in the condensation of water vapor. The samples that are oily wastes or waste oils and that can pass through the filter can conveniently be diluted with an appropriate solvent (Method 3585) and injected directly into a GC/MS system for analysis. Hexadecane is used as a solvent in this method. The volatile organic compounds in soils and other solid samples can be measured by what is known as automated headspace method (Method 5021). In this method, the sample is placed in a tared septum-sealed vial. A matrix modifier containing internal and/or surrogate standards is added into it. The sample vial is then heated in an automated equilibrium headspace sampler at 85°C while its contents mixed by mechanical vibration. A measured volume of the headspace from the vial is then introduced automatically into the GC or GC/MS system for analysis.

Air Analysis

Volatile organic compounds in air can be analyzed by U.S. EPA Method TO-14A or by NIOSH methods. The latter especially applies to workplace indoor air involving occupational exposures. One or more than one such NIOSH methods may be used to measure volatile organic compounds depending on the chemical nature and/or the chemical structures of such compounds. The NIOSH methods are simple and based on passing a measured volume of air using an air sampling pump through sorbent tubes that are packed with adsorbents such as activated charcoal, tenax, or silica gel and then desorbing out the adsorbed compounds into a suitable solvent followed by their analysis by GC or GC/MS. NIOSH Method 2549 details a screening procedure to measure several different classes of volatile organic compounds in air. U.S. EPA Method TO-14A and NIOSH Method 2549 are outlined below.

Several methods have been reported in the literature. Demeestere et al. (2007) have reviewed various sample preparation methods for VOC analysis in air. Sample preconcentration is a critical step in the air analysis. UV differential absorption spectroscopy is the only technique that allows the measurement of volatile compounds in the air without any sample preconcentration. However, this technique is limited to measure only a few compounds in the air. Preconcentration steps are needed when the concentrations of volatile compounds in the air are low. In general, such preconcentration can be carried out in two ways: (1) cryogenic trapping in a canister and (2) adsorptive sampling, either passive or active. When air is sampled by adsorptive methods, the volatile compounds are desorbed out from the adsorbent bed by either thermal or solvent desorption. Impingers may also be used to trap the compounds of interest. Air may be bubbled through a solution in an impinger. Compounds may as well be converted into their suitable derivatives for their analyses by reacting with appropriate derivatized agents coated onto the adsorbents or dissolved in solvents in impingers.

Cryogenic trapping using a canister requires the compounds to be transported onto the GC injector port with an inert carrier gas by using various techniques including gradual heating of the canister and/or applying vacuum. In cryogenic sampling, the volatile compounds in air are collected in a cooled tube usually filled with glass beads at temperatures ranging between −150°C and −170°C. Sampling may be carried out at other temperatures, such as in the temperature range of +10°C to −30°C in the presence of sorbent agents in Peltier-type cooling devices.

SPME techniques are alternative methods to preconcentrate volatile organic compounds in air. In these methods solid polymeric stationary phases, coated on fused silica fibers are used. Polydimethylsiloxane–Carboxen SPME fibers are known to be very efficient trapping media. The film thickness of stationary phase coatings may range usually from 5 to 100 um and the volume of the sorbent is usually less than 1 μL. Some commonly used stationary phases, such as Carboxen or PDMS that are available in a wide range of polarity. The preconcentration of analytes involve their partitioning between the sampled air and the stationary phases with liquid-like properties. In addition, the volatile organic compounds that are polar and reactive or thermally unstable may be derivatized into their stable derivatives. In addition, the SPME fiber may be directly introduced into a portable mass spectrometer for trace level detections of VOCs. This technique is known as fiber

introduction mass spectrometry (FIMS). Although the SPME methods have shown the potential for wide application, they too have certain limitations and disadvantages because of their limited sorption capacity due to the small volume of sorbent coating, possibility of bleeding of coating into the GC injector, and the limited lifetime of the fibers. Various sample preparation methods including SPME-based techniques have been well reviewed (Demeestere et al., 2007). Moxom et al. (2003) have reported a method to analyze several volatile organics in air using a micro-ion trap mass analyzer equipped with a sampling inlet of a semipermeable membrane. Van Berkel et al. (2008) have described a fast and noninvasive diagnostic procedure to measure volatile organic compounds in exhaled human air. Their method involves thermal desorption and GC coupled to time-of-flight mass spectrometry aimed to serve as noninvasive diagnostics of inflammatory diseases including pulmonary diseases.

U.S. EPA Method TO-14A

Air samples are collected at both subatmospheric as well as at high pressures in an initially evacuated canister attached to a pump-ventilated sample line. When sampling is carried out under pressure, an additional pump is used to provide positive pressure to the canister. A sample of ambient air is drawn into the canister and the canister valve is closed. The sample is transported to the laboratory for analysis. The canister is attached to an analytical system. Any water vapor present in the sample is removed by passing the air through a dryer. The volatile organic compounds in the air sample are then concentrated by collection in a cryogenically cooled trap. The cryogen is then removed and the temperature of the trap is raised to revolatilize the compounds. The compounds are transferred with a carrier gas onto a GC column, separated on the capillary column, and detected by a suitable GC detector or by a mass spectrometer and quantified. The GC detectors (or the multidetector system) may include one or more of the detectors such as ECD, PID, FID, and NPD depending on the compounds of interest or specific need. The compounds may alternatively be determined by a quadrupole mass spectrometer under the GC/MS/SCAN mode for positive identification and GC/MS/SIM mode for quantitation. Lower detection levels for compounds when analyzing by GC/MS can be achieved under the SIM mode. Alternatively, an ion trap detector can be used instead of a quadrupole detector in such GC/MS analysis (U.S. EPA Method TO-15).

The volatile compounds listed under this method are presented in Table 63.3 along with their CAS registry numbers, molecular formulas, and ion/abundance ratios. The synonyms or other common names of some of the compounds are also given below their names. These compounds are presented in the order of their increasing retention times under the GC conditions mentioned above and not in alphabetical order. It may be noted here that some other volatile substances that may be present in the sample but not listed in this method may also be determined by this procedure if they could be separated on the column, confirmed by mass spectroscopy, and their measurements meet the QC criteria. Under the ion/abundance column, the primary mass ion for the specific compound would be the base peak with highest abundance (normalized to 100%) and the abundances of the secondary mass ions are given as the ratios to their primary ion base peaks, respectively. For example, the primary mass ion of Freon-12 with the highest peak (base peak) is at 85 while the abundance of the secondary mass ion at 87 should be about 31% of the abundance of the primary ion.

All the characteristic mass ions of isomers of xylene and also those of dichlorobenzene are same. Such isomers may be identified from their retention times but not from their identical mass spectra. However, these and a few other compounds listed above may coelute on a packed column.

In addition, ambient air may be analyzed on site for volatile organic compounds by a portable gas chromatograph equipped with a PID. This method may be used to screen the presence of contaminants in the air to provide qualitative information regarding the substances detected and it should not be used for quantitation. An accurate volume of ambient air is drawn through a sampling port and into a concentrator and then transported by carrier gas onto a packed column and into a PID. The compounds are separated on a column of 0.66 m length and 3.2 mm internal diameter packed

TABLE 63.3
Volatile Organic Compounds by U.S. EPA Method TO-14A

Compounds/CAS No Synonyms	Formulas	Ion/Abundance (amu/100% Base Peak)
Freon-12 [75-71-8] (dichlorodifluoromethane)	Cl_2CF_2	85/100 87/31
Methyl chloride [74-87-3] (chloromethane)	CH_3Cl	50/100 52/34
Freon-114 [76-14-2] (1,2-dichloro-1,1,2,2-tetrafluoroethane)	$ClCF_2CClF_2$	85/100 135/56, 87/33
Vinyl chloride [75-01-4] (chloroethene)	$CH_2{=}CHCl$	62/100 27/25, 64/32
Methyl bromide [74-83-9] (bromomethane)	CH_3Br	94/100 96/85
Ethyl chloride [75-00-3] (chloroethane)	CH_3CH_2Cl	64/100 29/40, 27/40
Freon-11 [75-69-4] (trichlorofluoromethane)	CCl_3F	101/100 103/67
Vinylidene chloride [75-35-4] (1,1-dichloroethene)	$C_2H_2Cl_2$	61/100 96/55, 63/31
Dichloromethane [75-09-2] (methylene chloride)	CH_2Cl_2	49/100 84/65, 86/45
Freon-113 [76-13-1] (1,1,2-trichloro-1,2,2-trifluoroethane)	CF_2ClCCl_2F	151/100 101/40, 103/90
1,1-Dichloroethane [75-34-3] (ethylidene chloride)	CH_3CHCl_2	63/100 27/64, 65/33
cis-1,2-Dichloroethylene [156-59-2]	$CHCl{=}CHCl$	61/100 96/60, 98/44
Chloroform [67-66-3] (trichloromethane)	$CHCl_3$	83/100 85/65, 47/35
1,2-Dichloroethane [107-06-2] (ethylene dichloride)	$ClCH_2CH_2Cl$	62/100 27/70, 64/31
1,1,1-Trichloroethane [71-55-6] (methyl chloroform)	CH_3CCl_3	97/100 99/64, 61/61
Benzene [71-43-2] (cyclohexatriene)	C_6H_6	78/100 77/25, 50/35
Carbon tetrachloride [56-23-5] (tetrachloromethane)	CCl_4	117/100 119/97
1,2-Dichloropropane [78-87-5] (propylene dichloride)	$CH_3CHClCH_2Cl$	63/100 41/90, 62/70
Trichloroethylene [79-01-6] (trichloroethene)	$ClCH{=}CCl_2$	130/100 132/92, 95/87
cis-1,3-Dichloropropene [10061-01-5] (*cis*-1,3-dichloropropylene)	$CH_3CCl{=}CHCl$	75/100 39/70, 77/30
trans-1,3-Dichloropropene [10061-02-6] (*trans*-1,3-dichloropropylene)	$ClCH_2CH{=}CHCl$	75/100 39/70, 77/30
1,1,2-Trichloroethane [79-00-5]	$CH_2ClCHCl_2$	97/100 83/90, 61/82
Toluene [108-88-3] (methyl benzene)	$C_6H_5CH_3$	91/100 92/57

(*Continued*)

TABLE 63.3 (*Continued*)
Volatile Organic Compounds by U.S. EPA Method TO-14A

Compounds/CAS No Synonyms	Formulas	Ion/Abundance (amu/100% Base Peak)
1,2-Dibromoethane [106-93-4] (ethylene dibromide)	$BrCH_2CH_2Br$	107/100 109/96, 27/15
Tetrachloroethylene [127-18-4] (perchloroethylene)	$Cl_2C{=}CCl_2$	166/100 164/74, 131/60
Chlorobenzene [108-90-7] (phenyl chloride)	C_6H_5Cl	112/100 77/62, 114/32
Ethylbenzene [100-41-4]	$C_6H_5C_2H_5$	91/100 106/28
m-Xylene [108-38-3] (1,3-dimethylbenzene)	$1,3\text{-}(CH_3)_2C_6H_4$	91/100 106/40

with 3% SP-2100 on 100/120 Supelcoport. Any equivalent column may alternatively be used. The airflow is 30 mL/min. The retention times of the peaks in the sampled air are compared to those in a standard chromatogram. A portable GC with multidetectors may be used to screen air toxics.

In the above method, purified "zero air," that contains no more than 0.1 ppm of the total hydrocarbons should be used as the carrier gas. Aluminum cylinders containing such purified zero air are commercially available. Other materials and reagents required for the analysis of volatile organic compounds in air by this method include high purity nitrogen gas for blank injections (small disposable cylinders are commercially available), gas-tight syringes without attached shut-off valves (Hamilton Model 1002LT, or equivalent), and a system performance mixture. The latter consists of a mixture of three target compounds, such as benzene, trichloroethylene, and styrene in nitrogen at a concentration of about 10 ppb each to monitor the performance of the instrument. This mixture is manufactured in small disposable gas cylinders at a pressure of 40 psi (275 kPa) and sold commercially. A portable gas chromatograph, Photovac Model 10S10, 10S50, or equivalent with a PID or with multidetectors or similar equivalent instrument may be used for the analysis.

U.S. EPA's Solid Wastes 846 Methods

U.S. EPA's Solid Wastes 846 also discusses sampling and analyses of selected volatile organic compounds in air. Method 0040 involves collecting air in a Tedlar bag and introducing the sampled air directly onto a GC using a sample loop. While Method 0030 uses resin/charcoal for trapping volatile organic compounds in the air, Method 0031 uses resin/Anasorb 747 for sampling. The organic compounds in both these methods are then measured by Method 5041 (purge and trap technique). Many volatile aldehydes including formaldehyde and ketones may be determined by Methods 0011 and 0100. In both these methods, the aldehydes and ketones are derivatized with 2,4-dinitrophenylhydrazine (DNPH) into their corresponding dinitrophenylhydrazone derivatives. While the former method employs an aqueous solution of DNPH through which air is bubbled the latter uses DNPH-coated silica gel. The DNPH derivatives of aldehydes and ketones are extracted out from water or the adsorbent using an appropriate solvent and analyzed by GC.

NIOSH Method 2549

This screening method is applicable to measure many types of volatile organic compounds in the air. A personal sampling pump is used to sample between 1 and 6 L of air at a flow rate ranging

from 0.01 to 0.05 L/min. The compounds are trapped over multibed sorbent tubes containing the sorbents, usually graphitized carbons and carbon molecular sieve. Such multibed sorbents should be capable of trapping organic compounds in the range of C_3–C_{16}. The multibed sorbents used in this method consist of Carbopack Y (40/60 mesh) 90 mg, Carbopack B (40/60 mesh) 115 mg, and Carboxen 1003 (40/60 mesh) 150 mg, separated by silanized glass wool. The adsorbed compounds are desorbed out by heating the sorbent bed at 300°C for 10 min under the flow of helium at 10 psi. The temperature of the transfer line is maintained at 150°C. An automated thermal desorption system, such as Perkin–Elmer ATD 400 or equivalent can be used for this purpose. The thermal desorption unit is interfaced to a GC/MS system for the analysis of compounds. The compounds are separated on a GC capillary column and identified by a mass spectrometer. The GC and the MS conditions used in the method are given below. Other equivalent columns and conditions may be used if those satisfy the requirements.

GC COLUMN AND CONDITIONS

DB-1 fused silica capillary column, 30 m length, 0.25 mm ID, 1 um film thickness; oven temperature, 35°C for 4 min, 8°C/min to 100°C, 15°C/min to 300°C, hold 1–5 min at 300°C.

MS CONDITIONS

Electron-impact ionization mode; scan 20–300 amu; transfer line temperature −280°C.

The volatile compounds listed under this method along with the class they belong to are presented in Table 63.4. All these compounds are identified from their mass spectra and retention times. Other compounds that are of similar chemical nature and with their boiling points and the vapor pressures in the same range may also be analyzed by this method. The most common alternative names of some of these compounds in Table 63.4 are shown next to them in parentheses. The characteristic mass ions of most of these compounds are presented elsewhere in this chapter and are not shown below. The CAS registry numbers are also omitted from Table 63.4 and can be found elsewhere in this text.

In addition to Method 2549 outlined above for screening volatile organic compounds in air, several other NIOSH methods may be used to measure specific compounds or different classes of volatile organics. These methods mostly involve passing a measured volume of air through sorbent

TABLE 63.4
NIOSH Method 2549 for Screening VOCs in Air

Class of Organics	Compounds/Synonyms
Aliphatic hydrocarbons	*n*-Pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-decane
Aromatic hydrocarbons	Benzene, toluene (methylbenzene), xylenes (dimethylbenzene)
Halogenated hydrocarbons	Methylene chloride (dichloromethane), 1,1,1-trichloroethane, perchloroethylene (tetrachloroethylene), 1,2-dichlorobenzene, 1,4-dichlorobenzene, Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane)
Aldehydes	Hexanal (hexaldehyde), nonanal, benzaldehyde
Ketones	Acetone (2-propanone), cyclohexanone, methyl ethyl ketone (2-butanone, MEK), methyl isobutyl ketone (MIBK)
Alcohols	Methanol (methyl alcohol), isopropanol (isopropyl alcohol), butanol (butyl alcohol)
Acetates	Ethyl acetate, butyl acetate, amyl acetate (banana oil, pentyl acetate)
Phenols	Phenol, *o*-cresol (2-methylphenol), *m*-cresol (3-methylphenol), *p*-cresol (4-methylphenol)
Glycol ethers	2-Butoxy ethanol (butyl cellosolve), diethylene glycol ethyl ether (carbitol)
Terpenes	*alpha*-Pinene, *beta*-pinene, *d*-limonene, turpentine (mixture of pinenes)
Siloxanes	Octamethylcyclotetrasiloxane

TABLE 63.5
Miscellaneous and Alternative NIOSH Methods for Some Volatile Organic Compounds in Air

NIOSH Methods	Compounds/Class
1000	Allyl chloride (halogenated hydrocarbon)
1001	Methyl chloride (halogenated hydrocarbon)
1003	Halogenated hydrocarbons
1007	Vinyl chloride (halogenated hydrocarbon)
1008	Ethylene dibromide (halogenated hydrocarbon)
1009	Vinyl bromide (halogenated hydrocarbon)
1010	Epichlorohydrin (chloroepoxide)
1011	Ethyl bromide (halogenated hydrocarbon)
1013	Propylene dichloride (halogenated hydrocarbon)
1014	Methyl iodide (halogenated hydrocarbon)
1015	Vinylidene chloride (halogenated hydrocarbon)
1016	Chlorofluoroethanes (fluorocarbon)
1018	Dichlorodifluoromethane (fluorocarbon)
1022	Trichloroethylene (halogenated hydrocarbon)
1024	1,3-Butadiene (conjugated olefin)
1025	Bromopropane isomers (halogenated hydrocarbon)
1300	Ketones (acetone, cyclohexanone, 2-pentanone, diisobutyl ketone, methyl isobutyl ketone)
1400	Alcohols (ethanol, 2-propanol, *tert*-butanol)
1401	Alcohols (1-propanol, 1- and 2-butanol, isobutanol)
1402	Alcohols (some C_3–C_5–alcohols, cyclohexanol)
1403	Glycol ethers (2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol)
1500	Hydrocarbons boiling between 36°C and 216°C, including alkanes from pentane to dodecane and cyclohexane, cyclohexene and methylcyclohexane
1501	Aromatics including benzene, toluene, isomers of xylene, cumene, styrene, and methylstyrenes
1550	Naphtha hydrocarbons in kerosene, petroleum ether, mineral spirits, and Stoddard solvent
1600	Carbon disulfide
1602	Dioxane (oxygen heterocycle)
1603	Acetic acid (carboxylic acid)
1604	Acetonitrile (nitrile)
1606	Acrylonitrile (nitrile)
1608	Glycidol (epoxy alcohol)
1609	Tetrahydrofuran (oxygen heterocycle)
1610	Diethylether (ether)
1611	Methylal (aldehyde)
1612	Pyridine (nitrogen heterocycle)
1614	Ethylene oxide (oxirane)
2000	Methanol (alcohol)
2008	Chloroacetic acid (haloacetic acid)
2516	Dichlorofluoromethane (fluorocarbon)
2519	Ethyl chloride (halogenated hydrocarbon)
2520	Methyl bromide (halogenated hydrocarbon)
3700	Benzene (aromatic), by portable GC-PID
3701	Trichloroethylene, by portable GC-PID
3704	Tetrachloroethylene (halogenated hydrocarbon) (Tedlar air bag, direct injection, portable GC-PID)
4000	Toluene (aromatic hydrocarbon)

Note: Fluorocarbons are used as refrigerants. These compounds also belong to the class of halogenated hydrocarbons. However, they are classified under this header only to distinguish their source and exposure risk.

tubes and eluting the adsorbed organics with a suitable solvent followed by their analyses by a GC. Activated charcoal is mostly used as the adsorbent in such methods. Compounds are usually desorbed with carbon disulfide and measured by GC-FID. For the polar analytes, such as aldehydes or alcohols, silica gel is the adsorbent of choice. Other solvents are used for desorption, especially for the polar analytes in some methods. Table 63.5 lists some of these methods with their method numbers and the compound names and/or their classes. Detailed descriptions of these methods are presented in various chapters in this book under their respective classes.

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Section III

Selected Individual Compounds

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64 Acetaldehyde

Synonyms: ethanal, acetic aldehyde; formula: CH_3CHO; MW 44.05; CAS [75-07-0]; used in the production of acetic acid, acetic anhydride, and many synthetic derivatives; found in water stored in plastic containers; colorless mobile liquid; fruity odor when diluted; boils at 20.8°C; solidifies at −121°C; highly volatile; vapor pressure 740 Torr at 20°C; density 0.78 g/mL at 20°C; soluble in water, alcohol, acetone, ether, and benzene; highly flammable.

ANALYSIS OF AQUEOUS SAMPLE

- Aqueous samples heated in a purging vessel under helium purge. Analyte trapped over an adsorbent (i.e., silica gel or Tenax), then thermally desorbed out from the absorbent trap and transported onto a polar GC column for FID or GC/MS determination.
  - Purging efficiency low because of high solubility of the analyte in water.
- Aqueous samples buffered with citrate and pH adjusted to 3. Acidified sample derivatized with 2,4-DNPH; derivative analyzed by GC-NPD or reverse phase HPLC with UV detection at 360 nm.
  - For HPLC analysis, extract the derivative with methylene chloride and solvent exchange to acetonitrile.
  - HPLC column: A C-18 reverse phase column such as Zorbax ODS or equivalent.
  - GC column: A polar or an intermediate polar column (PEG-type phase) such as Carbowax 20 M, Supelcowax 10, DBWax, VOCOL, or equivalent; SPB-1, DB-1, or DB-5 columns are also suitable.
  - Samples must be collected without headspace, refrigerated, and analyzed within 7 days.

AIR ANALYSIS

- Air drawn through a midget impinger containing 0.05% DNPH reagent in dilute HCl and isooctane (immisicible); derivative formed partitions into isooctane; the organic solvent evaporated to dryness under a stream of N_2; residue dissolved in methanol and analyzed by HPLC (U.S. EPA Method TO5, 1988); recommended airflow rate 250 L/min; sample volume 25 L.
- Alternatively, acidified DNPH coated silica gel or florisil use as adsorbent; derivative analyzed by HPLC (U.S. EPA Method TO11); recommended flow rate 500 mL/min; sample volume 100 L.
- Air drawn through a solid sorbent tube containing 2-(hydroxymethyl) piperidine on XAD-2 (450 mg/250 mg); oxazolidine derivative of acetaldehyde formed; derivative desorbed into toluene under ultrasonic condition; analyzed by GC-FID (NIOSH Method 2538, 1994; OSHA Method 68, 1988).

  (1 ppm acetaldehyde in air = 1.80 mg/m^3 at NTP)

REFERENCES

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Supplement. 1988, US EPA, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina.

National Institute for Occupational Safety and Health. 1994. *NIOSH Manual of Analytical Methods*, 4th edn. Cincinnati, OH: National Institute for Occupational Safety and Health.

Occupational Safety and Health Administration. 1988. *OSHA Method 68*, OSHA Analytical Laboratory, Salt Lake Technical Center, Salt Lake City, Utah.

65 Acetone

Synonyms: 2-propanone, dimethyl ketone; formula: CH_3COCH_3; MW 58.08; CAS [67-64-1]; used as a common solvent in many organic syntheses and in paint and varnish removers; colorless liquid; characteristic odor; sweetish taste; boils at 56.5°C; vapor pressure 180 Torr at 20°C; freezes at −94°C; density 0.79 g/mL at 20°C; readily mixes with water and organic solvent; highly flammable.

ANALYSIS OF AQUEOUS SAMPLES

- Aqueous samples purged by an inert gas; analyte trapped on a sorbent trap; transferred onto a GC column by heating the trap and backflushing with helium; determined by GC/MS.
  - Purging efficiency of acetone is poor, because of its high solubility in water. The purging vessel should be heated.
  - The characteristic masses for GC/MS identification: 43 and 58.
  - GC column: Carbowax 20 M, Carbopack, or a fused silica capillary column, such as DB-5, SPB-5, or equivalent.
- Alternatively, an aliquot of aqueous sample directly injected onto an appropriate GC column for FID determination.
  - The detection range on the FID by direct injection without sample concentration is several orders higher than the purge and trap method (when purging vessel is heated).
- Trace acetone in water may be determined by a fast HPLC method (Takami et al., 1985); aqueous sample passed through a cartridge packed with a moderately sulfonated cation-exchange resin charged with 2,4-dinitrophenylhydrazine (DNPH); DNPH derivative eluted with acetonitrile and analyzed by HPLC with a 3 mm ODS column.
  - Precision and accuracy data for all the three above-mentioned methods not available.

AIR ANALYSIS

- Air drawn through a midget impinger containing 10 mL of 2 N HCl/0.5% DNPH and 10 mL of isooctane; the stable DNPH derivative formed partitions into the isooctane layer; isooctane layer separated; aqueous layer further extracted with 10 mL of 70/30 hexane/methylene chloride; the latter combined with isooctane; the combined organic layer evaporated under a steam of N_2; residue dissolved in methanol; the DNPH derivative determined by reversed phase HPLC using UV detector at 370 nm (U.S. EPA Method TO-5, 1988).
  - Recommended airflow rate 0.1 L/min; sample volume 20 L.
  - Isooctane must not completely evaporate out during sampling.
  - Calibration standards are prepared in methanol from solid DNPH derivative of acetone.
  - The molecular weight of DNPH derivative of acetone is 238.
  - HPLC column: Zorbax ODS; mobile phase: 80/20 methanol/water, flow rate 1 mL/min.
- Alternatively, a measured volume of air drawn through a prepacked cartridge coated with acidified DNPH; the DNPH derivative of acetone eluted with acetonitrile and measured by HPLC-UV as above (U.S. EPA Method TO-11, 1988).

- Alternatively, a measured volume of air drawn through a sorbent tube containing coconut shell charcoal (100 mg/50 mg); the analyte desorbed with CS_2 and analyzed by GC-FID (NIOSH Method 130D, 1984); recommended airflow rate 100 mL/min; sample volume 3 L.
  - GC column: 10% SP-2100 or DB-1 fused silica capillary column or equivalent.

  (1 ppm acetone in air = ~2.37 mg/m^3 at NTP)

REFERENCE

Takami, K., Kuwata, K., Sugimae, A., and M. Nakamoto. 1985. Trace determination of aldehydes in water by high performance liquid chromatography. *Anal. Chem.*, 57: 243–245.

66 Acetonitrile

Synonyms: methyl cyanide, cyanomethane; formula: CH_3CN; MW 41.06; CAS [75-05-8]; used as a solvent for polymers; boils at 81.6°C; solidifies at −45.7°C; vapor pressure 73 Torr at 20°C; density 0.786 g/mL at 20°C; readily mixes with water and most organic solvents; immiscible with petroleum fractions and some saturated hydrocarbons; flammable.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples directly injected onto a GC column, and determined by FID.
- Alternatively, sample subjected to purge and trap concentration; analyte determined by GC-FID, GC-NPD in N-mode, or GC/MS.
  - Poor purging efficiency at room temperature due to high solubility of analyte in water, resulting in low recovery and high detection level; purging chamber must be heated.
  - GC column: packed Porapak-QS (80/100 mesh) or Chromosorb 101 (60/80 mesh) or equivalent; capillary: 30–75 m length, 0.53 or 0.75 mm (or lower ID in conjunction with lower thickness) and 1.0 or 1.5 μm film VOCOL, DB-624, Rtx-502.2, DB-5, SPB-5, or equivalent.
- Alternatively, sample analyzed by HPLC; UV detection recommended at 195 nm; HPLC column: Zorbax ODS or equivalent; mobile phase water, flow rate 1–2 mL/min.
- Soil, sediments, or solid waste mixed with water and subjected to purge and trap concentration; aqueous extract may directly be injected onto GC, sample/extract analyzed as above.
- Alternatively, sample aliquot thermally desorbed under the purge of an inert gas, analyte determined as above.
  - Characteristic masses for GC/MS determination: 41, 50, and 39.
  - Sample collected in glass vial without headspace, refrigerated, and analyzed within 14 days of collection.
  - Detection level: in the range of 1 μg/L for a 25 mL sample size determined by the purge and trap-GC-FID method.

AIR ANALYSIS

- Air drawn through solid sorbent tube containing coconut shell charcoal (400 mg/200 mg); analyte desorbed with benzene and determined by GC-FID (NIOSH Method 1606, 1984); recommended flow rate 100 mL/min; sample volume 10 L.
- Alternately, air condensed at liquid argon temperature; contents of the trap swept by a carrier gas onto the GC column for determination by FID or a mass spectrometer.

(1 ppm CH_3CN in air = ∼1.68 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Safety and Health. 1984. *NIOSH Manual of Analytical Methods*, 3rd edition and all updates. Cincinnati, OH: National Institute for Occupational Safety and Health.

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67 Acrolein

Synonyms: 2-propenal, acraldehyde, vinyl aldehyde; formula: $CH_2 = CH–CHO$ an aldehyde; MW 56.07; CAS [107-02-8]; used to control aquatic weed, algae, and slime, and in leather tanning; colorless, volatile liquid; boils at 53°C; freezes at −87°C; density 0.843 g/mL at 20°C; soluble in water; mixes with alcohol and ether.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted by the purge and trap method; volatile analyte thermally desorbed from the trap and swept onto a GC column for separation; detected by FID or GC/MS.
  - Purging efficiency may be poor as the analyte is soluble in water; purging chamber should be heated.
- Aqueous samples or aqueous extracts of nonaqueous samples analyzed by HPLC on a C-18 reverse phase column; analyte detected by UV at 195 nm; mobile phase, water; flow rate 2 mL/min; pressure 38 atm.
  - Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water, subjected to purge and trap concentration and analyzed as above.
  - Characteristic masses for GC/MS identification: 56, 55, and 58.

AIR ANALYSIS

- Air drawn through a solid sorbent tube containing 2-(hydroxymethyl)piperidine on XAD-2 (120 mg/60 mg); acrolein converted into 9-vinyl-1-aza-8-oxabicyclo[4.3.0]nonane; derivative desorbed with toluene (placed in ultrasonic bath) and measured by GC-NPD in N-specific mode (NIOSH, 1984, Method 2501); recommended flow rate 50 mL/min; sample volume 10 L.
- Air drawn through a midget impinger containing 10 mL of 2 N HCl/0.05% 2,4-dinitrophenyhydrazine (DNPH) and 10 mL of isooctane; aqueous layer extracted with hexane/methylene chloride (70:30) and combined with isooctane; combined extract evaporated to dryness, residue dissolved in methanol; derivative analyzed by reverse phase HPLC using UV detector at 370 nm (U.S. EPA, 1988, Method TO5); recommended flow rate 200 mL/min; sample volume 20 L air.
- Air drawn through a cartridge containing silica gel coated with acidified DNPH; derivative eluted with acetonitrile and determined using isocratic reverse phase HPLC with UV detection at 360 nm (U.S. EPA, 1988, Method TO11); recommended flow rate 1 L/min; sample volume 100 L.

(1 ppm acrolein in air = ∼2.3 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Safety and Health. 1984. *NIOSH Manual of Analytical Methods*, 3rd edition and all updates. Cincinnati, OH: National Institute for Occupational Safety and Health.

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68 Acrylonitrile

Synonyms: 2-propenenitrile, vinyl cyanide; formula: $CH_2 = CH–CN$; MW 53.06; CAS [107-13-1]; a liquid at room temperature; boils at 77.5°C; density 0.806 g/mL; readily soluble in alcohol and ether; solubility in water ~7%; flammable and toxic.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted by the purge and trap method; volatile analyte thermally desorbed from the trap and swept onto a GC column for separation; detected by FID, NPD, or by a mass spectrometer (MS).
  - Because of moderate solubility in water, purging efficiency may be poor, resulting in low recovery and a high detection level; purging chamber should be heated.
- Aqueous samples or aqueous extracts of nonaqueous samples directly injected onto a C-18 reverse phase column for HPLC analysis with UV detection at 195 nm (U.S. EPA Method 8316, 1994); mobile phase, water; flow rate 2 mL/min; pressure 38 atm.
- Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water; subjected to purge and trap concentration and analyzed as above.
  - Alternatively, aqueous and nonaqueous samples microextracted with *tert*-butyl ether; extract analyzed by GC or GC/MS.
  - Characteristic masses for GC/MS identification: 53, 52, and 51.
  - Limit of detection: in the range 0.1 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - GC column-packed: Porapak-QS (80/100 mesh), Chromosorb 101 (60/80 mesh), or equivalent; capillary: VOCOL, DB-624, Rtx-502.2, DB-5, SPB-5, or equivalent fused silica capillary column.
  - Detection level: in the range of 1 μg/L for the purge and trap concentration (for a 5 mL sample aliquot) and FID determination.
  - Sample collected in glass vial without headspace, refrigerated, and analyzed within 14 days of collection.

AIR ANALYSIS

- Adsorbed over coconut shell charcoal (100 mg/50 mg); desorbed with acetone–CS_2 mixture (2:98); analyzed by GC-FID (NIOSH, 1984, Method 1604); recommended flow rate 100 mL/min; sample volume 10 L.
- Alternatively, air drawn over carbon molecular sieve in a cartridge; cartridge heated at 350°C under the He purge; analyte desorbed and collected in a cryogenic trap and then flash evaporated onto a precooled GC column (−70°C) temperature programmed; determined by GC-FID or GC/MS; (U.S. EPA, 1988, Method TO2); recommended flow rate 0.5 L/min; sample volume 100 L.
- Alternatively, sample collected in a liquid argon trap; trap heated; sample vapors swept onto a precooled GC column for determination by FID, PID, or NPD (U.S. EPA 1988, Method TO3).

(1 ppm acrylonitrile in air at NTP = ~2.16 mg/m^3)

REFERENCES

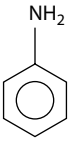
National Institute for Occupational Safety and Health. 1984. *NIOSH Manual of Analytical Methods*, 3rd edition and all updates. Cincinnati, OH: National Institute for Occupational Safety and Health.

US EPA. 1994. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, 3rd edn. Washington, DC: Office of Solid Wastes.

69 Aniline

DESCRIPTION

Synonyms: aminobenzene, phenylamine, benzenamine; formula: $C_6H_5NH_2$; structure:



MW 93.14; CAS [62-53-3]; used in the manufacture of dyes, varnishes, resins, pharmaceuticals, and photographic chemicals; colorless oily liquid with characteristic odor; boils at 184.5°C; freezes at −6°C; vapor pressure 0.3 Torr; density 1.02 g/mL at 20°C; moderately soluble in water 3.5% at 20°C; readily mixes with most organic solvents; weakly alkaline.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples made alkaline with NaOH to pH > 12; repeatedly extracted with methylene chloride, analyte partitions into methylene chloride that is separated, concentrated, and analyzed by GC-NPD or GC/MS.
  - GC column. Packed −3% SP-2250 on Supelcoport or equivalent; fused silica capillary column such as DB-5, PTE-5, or equivalent.
  - Characteristic masses for GC/MS determination: 93, 66, 65, and 39; peak intensities ratios: *m/z* 93:66:65 = 100:32:16.
  - Surrogates/IS: aniline-d_5 and nitrobenzene-d_5.
- Aniline at low ppm level may be directly analyzed by HPLC; detector, UV at 220 nm; mobile phase: acetonitrile–K_3PO_4 buffer at pH 6.5; column: Suplex pKb-100 or equivalent (Supelco, 1995).
- Soil, sediment, and solid waste samples mixed with anhydrous Na_2SO_4 and then methylene chloride; sonicated; extract cleaned by acid–base partitioning and analyzed as above.
  - Sample refrigerated and extracted within 7 days of collection and extract analyzed within 40 days.

AIR ANALYSIS

- Air drawn through a solid sorbent tube containing silica gel (150 mg/15 mg); analyte desorbed into 95% ethanol in an ultrasonic bath and determined by GC-FID or GC-NPD (NIOSH Method 2002, 1985); recommended flow rate 200 mL/min; sample volume 20 L.
  - High humidity reduces adsorption efficiency of silica gel.
  - Aniline stable in silica gel at least for 1 week.
  - Sensitivity is much greater on GC-NPD.
  - GC column: Chromosorb 103 (80/100 mesh) or equivalent.

  (1 ppm aniline in air = 3.8 mg/m^3 at NTP)

REFERENCE

Supelco Inc. 1995. Chromatography Products Catalog and Literature, Bellefonte, PA.

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70 Arsine

Synonyms: arsenic hydride, arsenic trihydride, hydrogen arsenide; formula: AsH_3; MW 77.95; CAS [7784-42-1]; used as a doping agent for solid-state electronic components; exposure risk arises from reaction of arsenic compounds with acids; colorless gas; disagreeable garlic odor; liquefies at −62°C; freezes at −117°C; gas density 2.70 g/L; slightly soluble in water (0.7 g/L); highly toxic.

AIR ANALYSIS

- Air drawn through a cellulose ester membrane (to remove any arsenic particulate) in front of a charcoal tube (100 mg/50 mg); arsine desorbed into 1 mL 0.01 M HNO_3 (in an ultrasonic bath for more than 30 min contact time); arsenic analyzed by graphite furnace atomic absorption spectrophotometer at the wavelength 193.7 nm (NIOSH Method 6001, 1985); recommended air flow rate 0.1 L/min; sample volume 5 L.
  - Multiply the concentration of arsenic by the stoichiometric factor 1.05 to calculate the concentration of arsine.
  - Use background correction for molecular absorption and a matrix modifier (Ni^{2+} solution).
  - The working range reported in the method is 0.001–0.2 mg/m^3 for a 10 L air sample.

    (1 ppm arsine in air = 3.19 mg/m^3 at NTP)

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71 Asbestos

Asbestos constitutes several types of hydrated silicate mineral fibers. The types of asbestos, their chemical compositions, and CAS Numbers are presented in Table 71.1. These substances occur in nature in rocks, silicate minerals, fibrous stones, and underground mines. This class of substances exhibits unique properties of noncombustibility, high resistance to acids, and high tensile strength for which they were widely used in many products, including floor and roofing tiles, cement, textiles, ropes, wallboards, and papers. Because of the health hazards associated with excessive exposure to asbestos, the use of these substances is currently banned.

ANALYSIS

Asbestos can be determined by several analytical techniques, including optical microscopy, electron microscopy, x-ray diffraction (XRD), light scattering, laser microprobe mass analysis, and thermal analysis. It can also be characterized by chemical analysis of metals by atomic absorption, x-ray fluorescence, or neutron activation techniques. Electron microscopy methods are, however, commonly applied for the analysis of asbestos in environmental matrices.

ANALYSIS OF AQUEOUS SAMPLES

- A measured volume of sample is filtered through a membrane filter. The filter is placed on a petri dish and dried on a bed of desiccant in a desiccator. A section of the filter from any quadrant of sample and blank filters are "prepared" and transferred to a transmission electron microscopy (TEM) grid. The fibers are identified and counted by TEM at 15,000–20,000 magnification.
  - Samples containing high concentration of asbestos should be diluted appropriately with particle-free water.
  - Use mixed cellulose ester or polycarbonate filter in the analysis.
  - The term "sample or blank preparation" refers to a series of steps pertinent to TEM analysis. These include filter fusing, plasma etching, carbon coating, and specimen washing. Some of these steps may not be required if polycarbonate filters are used.
  - The grids should be dried before placing in TEM.
  - The instrument must be calibrated regularly.
  - Perform a blank analysis for each batch using particle-free water, same reagents, and same type of filter.

TABLE 71.1
Asbestos Types and Their Compositions

Asbestos	CAS No.	Composition
Actinolite	[13768-00-8]	$2CaO \cdot 4MgO \cdot FeO \cdot 8SiO_2 \cdot H_2O$
Anthophyllite	[17068-78-9]	$7MgO \cdot 8SiO_2 \cdot H_2O$
Amosite	[12172-73-5]	$11FeO \cdot 3MgO \cdot 16SiO_2 \cdot 2H_2O$
Crocidolite	[12001-28-4]	$Na_2O \cdot Fe_2O_3 \cdot 3FeO \cdot 8SiO_2 \cdot H_2O$
Chrysotile	[12001-29-5]	$3MgO \cdot 2SiO_2 \cdot 2H_2O$
Tremolite	[14567-73-8]	$2CaO \cdot 5MgO \cdot 8SiO_2 \cdot H_2O$

- Do not use polypropylene bottles for sampling.
- Aqueous samples must be analyzed within 48 h of collection.
- Certain minerals can interfere in the test. They include halloysite, palygorskite, antigorite, hornblende, and others.
- The results are expressed as million fibers per liter (MFL) or million structures per liter (MSL).

AIR ANALYSIS

- Air is drawn through a 0.8–1.2 mm cellulose-ester membrane filter. The asbestos fibers are counted by positive phase-contrast microscopy technique. The sample is prepared by acetone/triacetin method (NIOSH Method 7400, 1994).
  - The sampling flow rate and time should be adjusted to produce a fiber density of 100–1300 fibers/mm^2.
  - A flow rate of 1–4 L/min for 8 h is appropriate for air containing less than 0.1 fiber/mL. Sample volume should be lower in a dusty atmosphere.
  - The method does not measure asbestos fibers less than 0.25 mm diameter.
  - Alternatively, asbestos fibers collected on the filter counted by TEM, following the modified Jaffe wick technique for sample preparation (NIOSH Method 7402, 1987).
  - The method can measure the asbestos fibers of the smallest diameter (<0.05 mm).
- Percent chrysotile asbestos in bulk samples may be measured by x-ray powder diffraction (NIOSH Method 9000, 1984); sample dust grinded under liquid N_2; wet sieved through 10 mm sieve; sieved material treated with 2-propanol; agitated in an ultrasonic bath; filtered on a silver filter; measured by XRD, using a Cu target x-ray tube.

REFERENCE

National Institute for Occupational Health and Safety. 1994. NIOSH Manual of Analytical Methods, 4th edn. Cincinnati, OH: National Institute for Occupational Health and Safety.

72 Benzene

Synonyms: benzol, cyclohexatriene; formula: C_6H_6; structure:

MW 78.12; CAS [71-43-2]; occurs in gasoline and coal-tar distillation products; used as a solvent and in organic synthesis; colorless liquid with characteristic odor; boils at 80.1°C; freezes at 5.5°C; vapor pressure 76 Torr at 20°C; density 0.88 g/L; slightly soluble in water (1.78 g/L); readily miscible with organic solvents; toxic and carcinogenic; flammable.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Analysis by the purge and trap method; a measured volume of sample purged with helium in a purging vessel; benzene collected on the sorbent trap thermally desorbed from the trap and swept by an inert gas onto a GC column for separation from other volatile compounds and detection by PID, FID, or a mass spectrometer (MS).
- Solid samples mixed with water or methanol; an aliquot of aqueous extract or a portion of methanol extract spiked into water and measured into the purging vessel; subjected to purge and trap concentration and analyzed as above.
- Alternatively, benzene thermally desorbed from the solid matrix under the He purge (without any solvent treatment) and analyzed by GC or GC/MS as above.
  - Characteristic masses for GC/MS identification: 78, 77, 52, and 39 (relative intensities of peaks *m*/*z* 78:77:52 = 100:20:19).
  - Limit of detection: in the range 0.5 μg/L when detected by PID for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: benzene-d_6 and fluorobenzene.
  - Samples collected in glass containers without headspace, refrigerated, and analyzed within 7 days; sample preserved with 1:1 HCl (0.2 mL acid per 40 mL sample) may be analyzed in 14 days.

AIR ANALYSIS

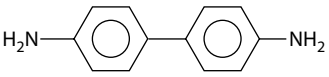
- Air collected in a Tedlar bag; 1 mL air directly injected onto GC (portable) for PID detection; flow rate 20–50 mL air/min (NIOSH Method 3700, 1987).
  - Analysis must be done within 4 h of sample collection.
- Air drawn through a sorbent tube containing coconut shell charcoal (100 mg/50 mg); analyte desorbed into CS_2 (on 30 min standing) and analyzed by GC-FID (NIOSH Method 1501, 1984); recommended flow rate 100 mL/min; sample volume 10 L.
  - GC column: packed column—10% OV-275 on 100/120 mesh Chromosorb W-AW, Porapak P 50/80 mesh, or equivalent.
- Air drawn through a cartridge containing Tenax (~2 g); cartridge heated under the He purge; benzene transferred into a cold trap and then to the front of a GC column at −70°C; column heated; analyte determined by GC/MS (U.S. EPA Method TO1); recommended flow rate 100 mL/min; sample volume 10 L.

- Adsorbed over carbon molecular sieve (~400 mg) in a cartridge; heated at 350°C under the He purge; transferred into a cryogenic trap and flash evaporated onto a capillary column; determined by GC/MS (U.S. EPA Method TO2); recommended flow rate 1 L/min; sample volume 100 L.
- Collected in a trap in liquid argon; the trap removed and heated; sample transferred to a precooled GC column for PID or FID detection (U.S. EPA Method TO-3).
- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into cryogenically cooled trap attached to a GC column; the trap heated; benzene determined by GC/MS (U.S. EPA Method TO-14).

(1 ppm benzene in air = ~3.2 mg/m^3 at NTP)

73 Benzidine

Synonyms: 4,4′-biphenyldiamine; 4,4′-diamino-1,1-biphenyl, *p*,*p*′-dianiline; formula: $C_{12}H_{12}N_2$; MW 184.26; structure:



CAS [92-87-5]; used in the past in the manufacture of dyes; no longer used in dyes because of its cancer-causing effect; white crystalline solid; melts at 120°C; boils at 400°C; slightly soluble in cold water (0.04%); moderately soluble in hot water, alcohol, and ether.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted with chloroform; chloroform extract further extracted with 1 M H_2SO_4; the acid extract buffered with 0.4 M sodium tribasic phosphate and then pH adjusted between 6 and 7 using NaOH; the neutralized extract then treated with chloroform; organic layer separated and concentrated; benzidine analyzed by HPLC using an electrochemical detector (i.e., glassy carbon electrode).
  - Analyte, if found, must be confirmed either by HPLC, setting electrochemical conditions at a second potential, or by GC/MS.
  - HPLC column: Lichrosorb RP-2 or equivalent, particle size 5 μm; mobile phase: acetonitrile/0.1 M acetate buffer (pH 4.7) (50:50).
  - Characteristic masses for GC/MS identification: 184, 92, and 185.
  - GC column: a packed column, such as 3% SP-2250 on Supelcoport or equivalent; or a fused silica capillary column such as DB-5, SPB-5, Rtx5, or equivalent.
  - MDL: in the range 0.1 μg/L by HPLC, when 1 L sample concentrated down to 1 mL, while approximately 50 μg/L by GC/MS with similar sample concentration.
  - Soil, sediment, and solid waste samples mixed with anhydrous Na_2SO_4 and extracted with chloroform by sonication; chloroform extract treated with acid, pH adjusted, and reextracted as above; analysis performed as above.
  - All samples stored at 4°C in glass containers; protected from light and air oxidation; extracted within 7 days of collection and analyzed within 7 days of extraction; residual chlorine if present in aqueous samples must be removed by adding $Na_2S_2O_3$ (∼100 mg/L sample).

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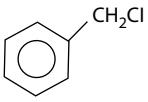
74 Benzyl Chloride

DESCRIPTION

Synonyms: (chloromethyl)benzene, tolyl chloride, α-chlorotoluene; formula: C_7H_7Cl; structure:



MW 126.59; CAS [100-44-7]; used in dyes, resins, perfumes, and lubricants; colorless liquid with pungent aromatic odor; boils at 179°C; freezes at −43°C; density 1.10 g/mL at 20°C; insoluble in water; miscible with most organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted by the purge and trap method; analyte thermally desorbed from the trap and swept onto a GC column for separation; detected by HECD, ECD, PID, or by a mass spectrometer.
- Alternatively, aqueous samples extracted with methylene chloride by LLE; extract concentrated and analyzed by GC using FID, PID, ECD, or by GC/MS.
- Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water, subjected to purge and trap concentration and analyzed as above.
  - Methanol extract may be directly injected onto the GC instead of the purge and trap concentration.
  - Solid matrices extracted with methylene chloride by sonication or Soxhlet extraction: extract concentrated and analyzed as above.
  - Characteristic masses for GC/MS identification: 91 and 126.
  - Limit of detection: in the range 0.1 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: 4-bromofluorobenzene and fluorobenzene.
  - Sample collected in glass/plastic containers without headspace, pH adjusted to <2 with 1:1 HCl (if not analyzed immediately), refrigerated, and analyzed within 14 days.

See Chapter 32 for GC columns and conditions and a detailed discussion.

AIR ANALYSIS

- Adsorbed over coconut charcoal (100 mg/50 mg); desorbed with CS_2 and analyzed by GC-FID; recommended flow rate 200 mL/min; sample volume 20 L.
- Adsorbed over Tenax (1–2 g) in a cartridge; analyte desorbed with an inert gas under heating and transferred onto a cold trap and then onto the front of a precooled GC column at 70°C; column heated; analyte eluted and detected by GC/MS, ECD, or FID; recommended flow rate 0.5 L/min; sample volume 100 L.
- Collected in a trap in liquid argon; the trap removed and heated; sample transferred to a precooled GC column for ECD or FID detection (U.S. EPA Method TO-3).

- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into a cryogenically cooled trap attached to a GC column; the trap heated; the analyte separated on the column for detection by ECD, FID, or GC/MS (U.S. EPA Method TO-14).

  (1 ppm benzyl chloride in air = ~5.2 mg/m^3 at NTP)

75 1,3-Butadiene

Synonyms: bivinyl, vinyl ethylene, biethylene; formula: C_4H_6; structure: $CH_2{=}CH{-}CH{=}CH_2$; MW 54.10; CAS [106-99-0]; petroleum product; used to produce synthetic rubber, elastomers, and food-wrapping materials; colorless gas, mild aromatic odor; heavier than air; gas density 1.865 (air = 1); 2.212 g/L at NTP; liquefies at −4.5°C; solidifies at −109°C; slightly soluble in water, 500 mg/L, soluble in organic solvents; carcinogenic; flammable.

AIR ANALYSIS

- Air drawn through a solid sorbent tube packed with coconut charcoal (400 mg/200 mg); 1,3-butadiene desorbed with 4 mL methylene chloride (more than 30 min standing); analyzed by GC-FID (NIOSH Method 1024, 1994); recommended air flow rate 0.2 L/min; sample volume 20 L.
  - The upper limit of the sampler is 100 ppm.
  - The presence of other hydrocarbons may interfere in the test. High humidity can affect sampling efficiency.
  - GC column: 10% FFAP on 80/100 mesh Chromosorb WAW. This column may not give adequate resolution from other hydrocarbons, C_4–C_6 compounds. A 50 m × 0.32 mm ID fused silica porous-layer open-tubular column coated with AL_2O_3/KCI gives better separation. Degradation of Al_2O_3 coating may be prevented by using a backflushable precolumn.
  - The sample (when the analyte remains adsorbed onto the trap) is stable for 3 weeks if stored at −4°C. At ambient temperature, the average loss was found to be 1.5% per day for 26 mg of 1,3-butadiene loaded on the adsorbent (NIOSH, 1994).

    (1 ppm 1,3-butadiene in air = 2.21 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Health and Safety. 1994. *NIOSH Manual of Analytical Methods*, 4th edn. Cincinnati, OH: National Institute for Occupational Health and Safety.

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76 Carbon Disulfide

DESCRIPTION

Synonym: dithiocarbonic anhydride; formula: CS_2; MW 76.13; CAS [75-15-0]; used in the manufacture of rayon and soil disinfectants and used as a solvent; colorless liquid with a strong foul odor; boils at 46.5°C; freezes at −111.6°C; density 1.263 g/mL at 20°C; slightly soluble in water (0.22% at 20°C); miscible with alcohol, ether, benzene, and chloroform; highly toxic and flammable (Patnaik, 2007).

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples concentrated by the purge and trap method; analyte determined by GC using a FPD or by GC/MS.
- Solid matrices extracted with methanol; methanol extract spiked to reagent grade water and the aqueous solution subjected to purge and trap concentration and analyzed as above.
- Alternatively, CS_2 thermally desorbed under the purge of an inert gas and analyzed as above.

AIR ANALYSIS

- Air drawn through a solid sorbent tube containing coconut shell charcoal (100 mg/50 mg) and anhydrous Na_2SO_4 (270 mg); analyte desorbed with benzene and determined by GC-FPD (NIOSH Method 1600, 1984); flow rate 0.01–0.2 L/min; sample volume 3–25 L.
  - GC column: 5% OV-17 on GasChrom Q or 5% OV-210 on Chromosorb G-HP or equivalent.
  - Water vapor interferes in the sampling and it is removed by Na_2SO_4 in the sorbent tube.

  (1 ppm CS_2 in air = 3.11 mg/m^3 at NTP)

REFERENCES

National Institute for Occupational Health and Safety. 1984. *NIOSH Manual of Analytical Methods*, 3rd edn. Cincinnati, OH: National Institute for Occupational Health and Safety.

Patnaik, P. 2007. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 3rd edn. New York: John Wiley and Sons.

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77 Carbon Monoxide

Formula: CO; MW 28.01; CAS [630-08-0]; produced when substances burn in insufficient air; occurs in automobile exhaust gases and closed confinements; high risk of exposure under fire conditions; a colorless gas with no odor; liquefies at −191.5°C; solidifies at −205°C; slightly soluble in water; soluble in alcohol, acetone, chloroform, and acetic acid; highly toxic.

AIR ANALYSIS

- Air collected in Tedlar bag or glass bulb and directly injected onto a GC column for TCD detection.
  - GC-TCD sensitivity low; a detection level of 500 ppm may be achieved by injecting 1 mL of air.
  - GC column (packed): Molecular Sieve 5A or Carboxen 1004 micropacked or equivalent in stainless steel column.
- Air drawn through a vacuum pump into the gas cuvette of a nondispersive infrared spectrophotometer; IR absorption by CO is measured using two parallel IR beams through the sample and reference cell and a selective detector; detector signal amplified; concentration of the analyte determined from a calibration curve prepared from standard calibration gases (ASTM Method D 3162–91, 1993).
  - Water vapor interferes in the test; air should be dried by passing through silica gel.
  - Many nondispersive IR air analyzers (such as Myran and other models) are commercially available for the continuous measurement of CO in the atmosphere.
  - Detection limit in IR method is much lower than in the GC-TCD; detection range 0.5–100 ppm.
- Diffusion type colorimetric dosimeters (such as Vapor Guard) give a direct readout of CO level without chemical analysis; a color forming reagent impregnated on purified silica gel; color changes from pale yellow to gray black and dosage exposure measured from the length of the stain.

(1 ppm carbon monoxide in air = 1.14 mg/m^3 at NTP)

REFERENCE

American Society for Testing and Materials. 1993. *Atmospheric Analysis in Annual Book of ASTM Standards*, Vol. 1, 11.03, Philadelphia, PA.

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78 Carbon Tetrachloride

Synonyms: tetrachloromethane, tetrachlorocarbon; formula: CCl_4; MW 153.81; CAS [56-23-5]; used as a solvent; colorless liquid with characteristic odor; boils at 76.7°C; freezes at −23°C; vapor pressure 89.5 Torr at 20°C; density 1.59 g/mL at 20°C; slightly soluble in water (∼800 mg/L); miscible with organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples subjected to the purge and trap concentration; CCl_4 thermally desorbed and swept onto a GC column for separation from other volatile compounds and detection by HECD, ECD, or MSD.
- Alternatively, microextraction with hexane and analysis by GC-ECD, precision and accuracy of the method not established.
- Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water, subjected to the purge and trap concentration and analyzed as above.
  - Characteristic masses for GC/MS identification: 117, 119, and 121.
  - Limit of detection: in the range 0.1 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: bromochloromethane and 1,2-dichloroethane-d_4.
  - Samples collected in glass/plastic containers without headspace, refrigerated, and analyzed within 14 days.

See Chapter 32 for GC columns and conditions and further discussion.

AIR ANALYSIS

- Adsorbed over coconut charcoal (100 mg/50 mg); desorbed with CS_2 and analyzed by GC-FID; recommended flow rate 100 mL/min; sample volume 15 L (NIOSH Method 1003).
- Adsorbed overTenax (∼2 g) in a cartridge; cartridge then heated and purged with He; compound transferred into a cold trap and then to the front of a GC column at −70°; column heated; CCl_4 detected by ECD or GC/MS; recommended flow rate 100 mL/min; sample volume 10 L (U.S. EPA Method TO-1).
- Adsorbed over carbon molecular sieve (∼400 mg) in a cartridge; heated at 350°C under the He purge; transferred into a cryogenic trap and flash evaporated onto a capillary column GC/MS; recommended flow rate 1 L/min; sample volume 100 L (U.S. EPA Method TO-2).
- Collected in a trap in liquid argon; the trap removed and heated; sample transferred to a precooled GC column for ECD or FID detection; (U.S. EPA Method TO-3).
- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into cryogenically cooled trap attached to a GC column; the trap heated; the analyte separated on the column for detection by ECD or GC/MS (U.S. EPA Method TO-14).

  (1 ppm CCl_4 in air = ∼6.3 mg/m^3 at NTP)

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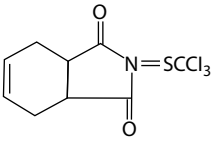
79 Captan

Synonym: *N*-(trichloromethylmercapto)-4-cyclohexene-1, 2-dicarboximide; formula: $C_9H_8Cl_3NO_2S$; structure:



MW 300.57; CAS [133-06-2]; crystalline solid; melts at 173°C; insoluble in water; slightly soluble in alcohol, ether, and hydrocarbons; soluble in chloroform and other halogenated solvents; used as a fungicide.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted with methylene chloride; solvent extract exchanged to hexane; extract cleaned up on a Florisil column; concentrated and analyzed by GC-ECD.
- Solid samples extracted with acetonitrile; extract diluted with water; the resulting solution mixed with methylene chloride–petroleum ether mixture (20:80) (A) and shaken; analyte partitions into (A); solvent layer (A) repeatedly washed with saturated NaCl solution; the extract then cleaned up on a Florisil column (first eluted with 200 mL solution A and then with a mixture of methylene chloride 50% and 1.5% acetonitrile in petroleum ether; eluant concentrated and diluted to the desired volume with petroleum ether; analyzed by GC-ECD (Pomerantz et al., 1970).
    - Detection level: in the range 0.1 mg/kg.

REFERENCE

Pomerantz, I.H., Miller, L.J., and G. Kava. 1970. Analysis of pesticide residues: Captan, Folpet and Difolatan, *J. Am. Oil Assoc.*, 53: 154.

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80 Chloroacetic Acid

Synonyms: monochloroacetic acid, chloroethanoic acid; formula $ClCH_2COOH$; MW 94.50; CAS [79-11-8]; used as a herbicide and in the manufacture of dyes; colorless or white crystals; occurring in three allotropic modifications: α, β, and γ; melts between 55°C and 63°C; boils at 189°C; very soluble in water; moderately soluble in alcohol, benzene, ether, and chloroform.

ANALYSIS OF AQUEOUS SAMPLES

- A 100 mL sample aliquot adjusted to pH 11.5; sample extracted with MTBE; chloroacetic acid partitions into aqueous phase; basic and neutral compounds in MTBE phase discarded; the aqueous phase now adjusted to pH 0.5 and extracted again with MTBE; the MTBE extract dried and concentrated; chloroacetic acid in the MTBE extract esterified with diazomethane; the methyl ester determined by capillary GC on an ECD (U.S. EPA Method 552, 1992a).
- Alternatively, a 30 mL sample portion is microextracted with a 3 mL aliquot of MTBE; the extract is esterified with diazomethane; the methyl ester of chloroacetic acid is analyzed on GC-ECD.
  - An alternate column must be used to confirm the presence of the analyte. A 30 m DB-1701 and DB-210 having 0.32 mm ID and 0.25–0.50 mm film thickness were used in the development of the U.S. EPA method.
  - The calibrations standards must be esterified prior to their injections into the GC.
  - 1,2,3-Trichloropropane was found to be a suitable internal standard.
  - The MTBE extract is concentrated down to 2 mL either at room temperature under a stream of dry N_2 or on a water bath at 35°C.
  - Chloroacetic acid is a strong organic acid that may react with alkaline substances and may be lost during the sample preparation. Glassware and glass wool must be acid rinsed with HCl (1 + 9); Na_2SO_4 must be acidified with H_2SO_4.
  - Many chlorinated compounds and organic acids may interfere in the GC-ECD analysis. Some basic and neutral interference can be removed by acid–base partitioning sample cleanup.
  - Unreacted diazomethane left after esterification should be removed by adding 0.2 g silica gel. Its presence is indicated from a persistent yellow color and effervescence due to N_2.
- Alternatively, a 100 mL sample portion that is pH adjusted to 5.0; chloroacetic acid separated on an anion exchange column and eluted with small aliquots of acidic methanol; a small volume of MTBE is then added as the cosolvent, resulting in esterification of the analyte; methyl ester partitions into the MTBE phase; the ester is analyzed by GC-ECD (U.S. EPA Method 552.1, 1992a).
  - Use LSE cartridge or disk as the anion exchange column. Add AG-1-X8 resin solution dropwise.
  - Condition the column by passing 10 mL aliquots of methanol, reagent water, 1 M HCl/methanol, reagent water, 1 M NaOH and reagent water, respectively, through the resin under vacuum at a rate of 2 mL/min. The resin bed must not be allowed to dry.
  - Sulfate, chloride, and other anions at high concentrations interfere in the test. Dilute the sample prior to analysis (1:5 or 1:10 dilution).

- Organic acids and phenols also interfere in the test. Perform a methanol wash after the acid analyte is adsorbed on the column.
- Samples dechlorinated with NH_4Cl and refrigerated at 4°C may be stable for 28 days.

See Chapter 31.

AIR ANALYSIS

- Air drawn through a solid sorbent tube containing silica gel (100 mg/50 mg) with glass wool plugs; analyte desorbed with 2 mL of deionized water; chloroacetate ion determined by ion chromatography with conductivity detection (NIOSH Method 2008, 1994); recommended air flow rate 0.1 L/min; air sample volume 25 L.
  - IC column: anion guard; anion separators in tandem packed with low-capacity anion exchange resin; anion suppressor packed with high-capacity cation exchange resin. Other IC column resins may be used, eluent: 1.5 mm $NaHCO_3$.
  - Standard solutions of chloroacetic acid in deionized water are to be used for the calibration.
  - Particulate salts of acids and chloroacetyl chloride interfere in the test.
  - The sample is stable for a week at room temperature and 30 days if refrigerated.
    - Working range for a 3 L air sample is 0.3–30 mg/m^3.

    (1 ppm chloroacetic acid in air = 3.86 mg/m^3 at NTP)

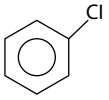
REFERENCES

National Institute for Occupational Safety and Health. 1994. *NIOSH Manual of Analytical Methods*, 4th edn. Cincinnati, OH: National Institute for Occupational Safety and Health.

US EPA. 1992. *Determination of Haloacetic Acids and Dalapon in Drinking Water by Ion-Exchange Liquid-Solid Extraction and Gas Chromatography with Electron Capture Detection*, Environmental Monitoring System Laboratory, Office of Research and Development, Cincinnati, OH.

81 Chlorobenzene

Synonyms: phenyl chloride, benzenechloride; formula: C_6H_5Cl; structure:



MW 112.56; CAS [108-90-7]; used in heat transfer medium and as a solvent in paint; colorless liquid with a faint almond odor; boils at 131°C; solidifies at −55°C; density 1.1 g/mL at 20°C; insoluble in water, miscible with organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted by the purge and trap method; volatile analyte thermally desorbed and swept onto a GC column for separation; detected by HECD, ECD, FID, or GC/MS.
- Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water, subjected to purge and trap concentration and analyzed as above.
  - Characteristic masses for GC/MS identification: 112, 77, and 114.
  - Limit of detection: in the range 0.02 mg/L when detected by PID or HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: 4-bromofluorobenzene and fluorobenzene.
  - Sample collected in glass containers without headspace, refrigerated, and analyzed within 14 days.

See in Chapter 32, three spacings for the GC columns and conditions, and a detailed discussion.

AIR ANALYSIS

- Adsorbed over coconut charcoal (100 mg/50 mg); desorbed with CS2 and analyzed by GC-FID; recommended flow rate: 200 mL/min; sample volume 20 L.
- Adsorbed over Tenax (1–2 g) in a cartridge; cartridge heated under He purge; analyte desorbed and transferred onto a cold trap and then onto a precooled GC column at −70°C; column heated; analyte eluted and detected by GC/MS, ECD, or FID; recommended flow rate 0.5 L/min; sample volume 100 L (U.S. EPA Method TO-1).
- Collected in a trap in liquid argon; the trap removed and heated; the sample transferred to a precooled GC column for ECD or FID detection (U.S. EPA Method TO-3).
- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into a cryogenically cooled trap attached to a GC column; the trap heated; the analyte separated on the column for detection by ECD, FID, or GC/MS (U.S. EPA Method TO-14).

(1 ppm chlorobenzene in air = ∼4.6 mg/m^3 at NTP)

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82 Chloroform

Synonyms: trichloromethane, methyl trichloride; formula: $CHCl_3$; MW 119.37; CAS [67-66-3]; a volatile halogenated solvent; boils at 61.2°C; vapor pressure 158 Torr at 20°C; heavier than water, density 1.484 g/mL at 20°C; solubility in water very low (1.2%), miscible in organic solvents; nonflammable.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples are subjected to the purge and trap concentration method; an aliquot of the sample is purged under helium flow chloroform and other volatile analyte thermally desorbed out from the sorbent trap and swept onto a GC column for separation; detected by HECD, ECD, or MSD.
- Aqueous samples extracted with hexane; extract injected onto the GC column for ECD detection; precision and accuracy of the method found to be low.
- Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water, subjected to the purge and trap concentration and analyzed as above.
  - Characteristic masses for GC/MS identification: 83 and 85.
  - Limit of detection: in the range 0.05 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: bromochloromethane and 1,2-dichloroethane-d_4.
  - Samples collected in glass/plastic containers without headspace, refrigerated, and analyzed within 14 days.

See Chapter 32 for GC columns and conditions and for a detailed analysis.

AIR ANALYSIS

- Adsorbed over coconut charcoal (100 mg/50 mg); desorbed with CS2 and analyzed by GC-FID; recommended flow rate 100 mL/min; sample volume 15 L (NIOSH Method 1001).
- Adsorbed over Tenax (~2 g) in a cartridge, which is then heated and purged with He; compound transferred into a cold trap and then to the front of a GC column at −70°C; column heated; $CHCl_3$ detected by ECD or GC/MS; recommended flow rate 100 mL/min; volume 10 L (U.S. EPA Method TO-1).
- Adsorbed over carbon molecular sieve (~400 mg) in a cartridge; heated at 350°C under He purge; transferred into a cryogenic trap and flash evaporated onto a capillary column GC/MS; recommended flow rate 2 L/min; sample volume 100 L (U.S. EPA Method TO-2).
- Collected in a trap in liquid argon; the trap removed and heated; sample transferred to a precooled GC column for ECD or FID detection (U.S. EPA Method TO-3).
- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into a cryogenically cooled trap attached to a GC column; the trap heated; the analyte separated on the column for detection by ECD, FID, or GC/MS (U.S. EPA Method TO-3).

  (1 ppm chloroform in air = 4.9 mg/m^3 at NTP)

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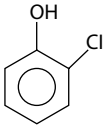
83 2-Chlorophenol

Formula: C_6H_5OCl; structure:



MW 128.56; CAS [95-57-8]; crystalline solid melting at 33.5°C; boils at 214°C; slightly soluble in cold water; soluble in organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- The pH of aqueous samples adjusted to below 2; extracted with methylene chloride; extract concentrated and analyzed by GC-FID or GC/MS.
  - Alternatively, extract exchanged into 2-propanol; derivatized with pentafluorobenzyl bromide, and determined by GC-ECD.
  - Aqueous samples may be analyzed by HPLC on an underivatized polystyrene–divinylbenzene column such as PolyRPCO (Alltech, 1995) or a C-18 reverse phase column; gradient: acetonitrile and 0.01 M K_3PO_4 at pH 7 (55:45) and the analyte detected by UV at 254 nm.
- Soil, solid waste, and sludge extracted with methylene chloride by sonication, Soxhlet, or supercritical fluid extraction; extract may be acid washed, concentrated, and analyzed by GC-FID, GC-ECD, or GC/MS as above.
  - Characteristic masses for GC/MS determination: 128, 64, and 130 (electron impact ionization); 129, 131, and 157 (chemical ionization).
  - Limit of detection: in the range 5–10 μg/L on FID or GC/MS and below 1 μg/L on ECD (for aqueous samples concentrated by 1000 times).
  - Recommended surrogate/IS: pentafluorophenol and 2-perfluoromethyl phenol.
  - Samples collected in glass containers, refrigerated, and extracted within 7 days of collection and analyzed within 40 days of extraction.

See Chapter 49 for GC columns and conditions.

AIR ANALYSIS

Recommended method: airborne particles collected on a sorbent cartridge containing polyurethane foam; extracted with 5% diethyl ether in hexane; extract analyzed by GC-ECD; recommended air flow 5 L/min; sample volume 1000 L.

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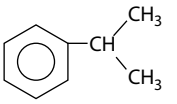
84 Cumene

Synonyms: isopropylbenzene, (1-methyl ethyl) benzene, 2-phenylpropane; formula: C_9H_{12}; structure:



MW 120.21; CAS [98-82-8]; used as a solvent and in organic synthesis; colorless liquid with an aromatic odor; boils at 152.5°C; vapor pressure 8 Torr at 20°C; freezes at −96°C; density 0.869 g/mL at 20°C; insoluble in water, miscible with organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Purge and trap method; a measured volume of sample purged with helium; vapors of cumene collected on a sorbent trap; cumene thermally desorbed from the sorbent trap and backflushed with helium onto a GC column for separation from other volatile compounds; determined by PID, FID, or a mass spectrometer.
- Solid samples mixed with methanol or acetone; an aliquot of solvent extract spiked into a measured volume of water (25 mL) in the purging vessel; subjected to purge and trap concentration and analyzed as above.
- Alternatively, cumene thermally desorbed from the solid matrix under the He purge (without any solvent treatment) onto the GC column and analyzed on a suitable detector.
  - Characteristic masses for GC/MS identification: 105 (primary ion) and 120.
  - GC column: a nonpolar fused silica capillary column, such as DB-5, VOCOL DB-624, or equivalent; packed column: 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent.
  - Limit of detection: in the range 0.2 mg/L for 25 mL sample analyzed by purge and trap GC/MS method.
  - Recommended surrogates/IS: ethylbenzene-d_5 (*m/z* 111) and pentafluorobenzene (*m/z* 168).
  - Samples collected in glass containers without headspace, refrigerated, and analyzed within 7 days of collection. Samples preserved with 1:1 HCl (0.2 mL acid/40 mL sample) may be analyzed in 14 days.

AIR ANALYSIS

- Air drawn through a sorbent tube packed with coconut shell charcoal (100 mg/50 mg); analyte desorbed into CS2 (more than 30 min standing); CS2 extract analyzed by GC-FID (NIOSH Method 1501, 1984); recommended air flow rate 100 mL/min; sample volume 20 L.
  - GC column: packed column 10% OV-275 on 100/120 mesh Chromosorb W-AW, Porapak P (50/80 mesh), or equivalent.
- (Suggested method): Alternatively air drawn through a cartridge packed with carbon molecular sieve (0.5 g); cartridge heated at 350°C under the He purge. Analyte transported to the front of a precooled GC column, temperature programmed; cumene separated on

the column and determined by a PID, FID, or a mass spectrometer; recommended air flow rate 0.5 L/min; sample volume 50 L.

- No precision and accuracy data available for this method.

(1 ppm cumene in air = 4.92 mg/m^3 at NTP)

REFERENCE

National Institute of Occupational Health and Safety. 1984. *NIOSH Manual of Analytical Methods*, 3rd edn. Cincinnati, OH: National Institute of Occupational Health and Safety.

85 Cyanogen

Synonyms: ethanedinitrile, oxalonitrile, oxalyl cyanide, dicyan; formula: $(CN)_2$; structure: N≡C–C≡N; MW 52.04; CAS [460-19-5]; used as a fuel gas, fumigant, and propellant; occurs in blast furnace gases; colorless gas; almond-like odor, becoming pungent at high concentration; liquefies at −21°C; highly soluble in water, alcohol, and ether; highly toxic and highly flammable.

AIR ANALYSIS (SUGGESTED METHOD)

- Air drawn through a 0.8 mm cellulose ester membrane (to separate cyanogen from particulate cyanide) followed by 0.1 N KOH bubbler solution; cyanide ion analyzed by cyanide ion-selective electrode; recommended flow rate 200 mL/min; sample volume 10 L.
  - No precision or accuracy data is available for the above method.
  - HCN may interfere in the test.
- Alternatively, air bubbled through a measured volume of methanol; the bubbler solution analyzed by GC-FID; peak areas compared against calibration standards for quantitation.
  - No precision or accuracy data are available for the above method.

  (1 ppm cyanogen = 2.13 mg/m^3 at NTP)

OSHA METHOD PV2104

Cyanogen in the air may also be analyzed by OSHA Method PV2104, a partially evaluated stopgap method. Samples are collected by drawing 3 to 12 L of air at a flow rate of 0.2 L/min through sampling tubes packed with XAD-2 adsorbent which have been coated with 10% (by weight) 2-(hydroxymethyl)piperidine. Cyanogen reacts with the coated reagent to form a derivative. Samples are then desorbed with toluene and analyzed by GC using nitrogen-phosphorus detector (NPD).

REFERENCE

Occupational Safety and Health Administration. 2004. *OSHA Method PV2104*, US Department of Labor, Washington, DC. www.OSHA.gov

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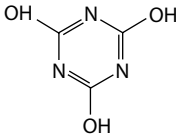
86 Cyanuric Acid

Synonyms: trihydroxycyanidine; 2,4,6-trihydroxy-1,3,5-triazine; formula: $C_3H_3N_3O_3$; structure:



MW 129.02; CAS [108-80-5] solid crystals that may occur as dihydrate; loses water of crystallization on exposure to air; evolves cyanic acid on heating; does not melt; slightly soluble in cold water (0.5%) but much more soluble in hot water; soluble in pyridine, hot alcohols, HCl, H_2SO_4, and caustic soda solution; insoluble in cold methanol, ether, benzene, acetone, and chloroform.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples buffered with Na_2HPO_4 and analyzed by HPLC–UV at 225 nm (see section Air Analysis).
- Aqueous samples may be directly injected into a GC column for FID determination; separation from other triazines, however, may be difficult.
  - Suggested GC column: DB-1701 or equivalent capillary column.
  - No precision and accuracy data available.
- Solid samples may be extracted with pyridine; extract analyzed by GC/MS.
  - Characteristic masses for GC/MS identification: 129, 43, 44, 86, and 70. Peak ratios: 129:43:44:86 = 100:59:56:15.
- Solid samples extracted with water; aqueous extract analyzed by HPLC–UV at 225 nm (see section Air Analysis).

AIR ANALYSIS

- Air drawn through 5 μm PVC membrane filter; analyte extracted with a mixture of 0.005 M Na_2HPO_4 in 5% methanol (95% water) at pH 7 in ultrasonic bath for 10 min; analyte detected by HPLC using an UV detector (at 225 nm) (NIOSH Method 5030, 1989).
  - HPLC column: μ-Bondapak C-18, 10 μm particle size. Mobile phase: Na_2HPO_4 (0.005 M) in methanol/water (5:95).

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87 Diazomethane

Synonym: azimethylene; formula: CH_2N_2; structure: $CH_2 = N^+ = N^-$; MW 42.04; CAS [334-88-3]; used as a methylating reagent in organic synthesis; yellow gas; liquefies at −23°C; solidifies at −145°C; decomposes on solid surfaces; soluble in ether and dioxane; solution unstable; readily breaks down to N_2; explodes on heating, rough surfaces, or in the presence of impurities, or when concentrated; highly toxic.

AIR ANALYSIS

- Air passed through a solid sorbent tube containing octanoic acid-coated XAD-2 resin (100 mg/50 mg); diazomethane converted to methyl octanoate; the product desorbed with CS_2 (more than 30 min contact time) and analyzed by GC-FID (NIOSH Method 2515, 1985); recommended flow rate 0.2 L/min; sample volume 20 L.
  - Multiply the concentration of methyl octanoate by the stoichiometric factor 0.266 to calculate the concentration of diazomethane.
  - GC column: SP-1000 on 100/120 mesh Chromosorb WHP, preceded by a precolumn packed with 10% Carbowax 20 M and 1.2% NaOH on 80/100 mesh Gas ChromQ.
  - Working range: 0.1–0.6 ppm for a 10 L air sample.

    (1 ppm diazomethane in air = 1.72 mg/m^3 at NTP)

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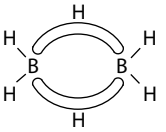
88 Diborane

Synonyms: boron hydride, boroethane; formula: B_2H_6; structure:



MW 27.69; CAS [19287-45-7]; used as a rocket propellant, a polymerization catalyst, a reducing agent, and in the vulcanization of rubber; colorless gas with a sweet, repulsive odor; liquefies at −92.5°C; freezes at −165°C; gas density 1.15 g/L; decomposes in water; soluble in CS_2; highly toxic and flammable; ignites in moist air.

AIR ANALYSIS

- Air drawn through a PTFE filter and then through a solid sorbent tube containing oxidizer-impregnated charcoal (100 mg/50 mg); adsorbent after sampling, transferred into 10 mL 3% H_2O_2; allowed to stand for 30 min and then placed in an ultrasonic bath for 20 min; diborane oxidized to boron; the latter measured at the wavelength 249.8 nm by plasma emission spectrometer using a DC plasma emission source (NIOSH Method 6006, 1987); recommended air flow rate 0.5–1 L/min; sample volume 100–250 L.
  - Use aliquots of 1% (v/v) diborane adsorbed on impregnated charcoal for calibration.
  - Multiply the concentration of boron as determined in the analysis by the stoichiometric factor 1.28 to calculate the concentration of diborane.
  - Boron may also be measured by inductively coupled plasma emission spectrometry (NIOSH Method 7300, 1989).
  - PTFE filter is used to remove boron-containing particulates. Use of mixed cellulose ester membrane prefilters is not recommended.
  - A blank analysis is performed on the media blanks for background correction.
  - The working range for a 250 L air sample is 0.1–0.5 ppm.
  - Avoid borosilicate glassware during sample preparation. Use plastic bottles, pipettes, and flasks.

    (1 ppm diborane = 1.131 mg/m^3 at NTP)

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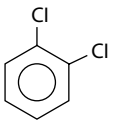
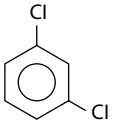
89 Dichlorobenzene

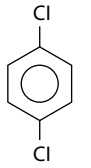
Formula: $C_6H_4C_{12}$; MW 147.00; structures of three isomeric forms as follows:



1,2-dichlorobenzene
(*o*-chlorobenzene)
(95-50-1)
(1)



1,3-dichlorobenzene
(*m*-chlorobenzene)
(541-73-1)
(2)



1,4-dichlorobenzene
(*p*-chlorobenzene)
(106-46-7)
(3)

1. Colorless liquid with faint odor, density 1.28 g/mL, boils at 179°C; freezes at −17°C.
2. Colorless liquid, density 1.29 g/mL; boils at 172°C; freezes at 124°C.
3. Colorless crystalline solid, sublimes at ambient temperature; melts at 54°C; boils at 174°C.

All these isomers are insoluble in water, soluble in organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted by the purge and trap method; sample purged with helium or nitrogen analyte thermally desorbed out of the trap and swept onto a GC column for separation; detected by HECD, ECD, PID, or a mass spectrometer.
  - Alternatively, extracted with methylene chloride by LLE; extract concentrated and analyzed by a GC using a PID, FID, ECD, or GC/MS.
- Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water; subjected to purge and trap concentration and analyzed as above.
  - Alternatively, extracted with methylene chloride by sonication or Soxhlet extraction; extract concentrated and analyzed.
  - Characteristic masses for GC/MS identification: 146, 111, and 148.
  - Limit of detection: in the range 0.1 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Elution pattern: 1,3-isomer followed by 1,4- and then 1,2-isomer, on a fused silica capillary column, for example, VOCOL.
  - Recommended surrogate/IS: 4-bromofluorobenzene and fluorobenzene.
  - Sample collected in glass containers without headspace, refrigerated, and analyzed within 14 days.

See Chapter 27 for GC columns and conditions and a detailed discussion.

AIR ANALYSIS

- Adsorbed over Tenax (1–2 g) in a cartridge; cartridge heated under the He purge; analyte desorbed and transferred onto a cold trap and then onto a precooled GC column at −70°C;

column heated; analyte eluted and determined by GC/MS, ECD, or FID; recommended flow rate 0.5 L/min; sample volume 100 L (U.S. EPA Method TO-1).

- Adsorbed over coconut charcoal (100 mg/50 mg); desorbed with CS_2 and analyzed by GC-FID; recommended flow rate: 200 mL/min; sample volume 20 L.
- Collected in a trap in liquid argon; the trap removed and heated; sample transferred to a precooled GC column for ECD or FID detection (U.S. EPA Method TO-3).
- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into cryogenically cooled trap attached to a GC column; the trap heated; the analyte separated on the column for detection by ECD, FID, or GC/MS (U.S. EPA Method TO-14).

(1 ppm dichlorobenzene in air $= \sim 6$ mg/m^3 at NTP)

90 1,1-Dichlorethylene

Synonym: vinylidene chloride; formula: $C_2H_2Cl_2$; structure: $Cl_2C = CH_2$.

MW 96.94; CAS[75-35-4]; colorless liquid; boils at 31.7°C; liquefies at −122.5°C; density 1.21 g/mL at 20°C; slightly soluble in water; miscible with organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Analyte in aqueous samples extracted by the purge and trap method; a measured volume of sample purged with helium; volatile analytes transferred into the vapor phase and trapped on a sorbent trap; analyte thermally desorbed and swept onto a GC column for separation from other volatile compounds; detected by HECD, ECD, or MSD.
- Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water; subjected to purge and trap concentration and analyzed as above.
  - Characteristic masses for GC/MS identification: 96, 61, and 98.
  - Limit of detection: in the range 0.15 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: bromochloromethane and 1,2-dichloroethane-d_4.
  - Samples collected in glass/plastic containers without headspace, refrigerated, and analyzed within 14 days.

See Chapter 27 for GC columns and conditions, and a detailed discussion.

AIR ANALYSIS

- Adsorbed over coconut charcoal (100 mg/50 mg); desorbed with CS_2 and analyzed by GC-FID; recommended flow rate 100 mL/min; sample volume 2 L.
- Adsorbed over carbon molecular sieve (~400 mg) in a cartridge; heated at 350°C under the He purge; transferred into a cryogenic trap and flash evaporated onto a capillary column GC/MS; recommended flow rate 2 L/min; sample volume 100 L (U.S. EPA Method TO-2).
- Collected in a trap in liquid argon; the trap removed and heated; sample transferred to a precooled GC column for ECD or FID detection (U.S. EPA Method TO-3).
- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into a cryogenically cooled trap attached to a GC column; the trap heated; the analyte separated on the column for detection by ECD, FID, or GC/MS (U.S. EPA Method TO-14).

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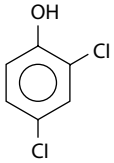
91 2,4-Dichlorophenol

Formula: $C_6H_4OCl_2$; structure:



MW 163.01; CAS [120-83-2]; crystalline solid melts a 45°C; boils at 210°C; insoluble in water; soluble in organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples pH adjusted below 2; extracted with methylene chloride; extract concentrated and analyzed by GC-FID or GC/MS.
  - Alternatively, extract exchanged into 2-propanol; derivatized with pentafluorobenzyl bromide, and determined by GC-ECD.
- Aqueous samples may be analyzed by HPLC on an underivatized polystyrene–divinylbenzene column such as PoIyRPCO (Alltech, 1995) or a C-18 reverse phase column; gradient: acetonitrile and 0.01 M K_3PO_4 at pH 7 (55:45) and the analyte detected by UV at 254 nm.
- Soil, solid waste, and sludge extracted with methylene chloride by sonication, Soxhlet, or supercritical fluid extraction; extract may be acid washed, concentrated, and analyzed by GC-FID, GC-ECD, or GC/MS as above.
  - Characteristic masses for GC/MS determination: 162, 164, and 98 (electron impact ionization); 163, 165, and 167 (chemical ionization).
  - Limit of detection: in the range 5–10 μg/L on FID or GC/MS and below 1 μg/L on ECD (for aqueous samples concentrated by 1000 times).
  - Recommended surrogate/IS: pentafluorophenol and 2-perfluoromethyl phenol.
  - Samples collected in glass containers, refrigerated and extracted within 7 days of collection and analyzed within 40 days of extraction.

See Chapter 44 for GC columns and conditions.

AIR ANALYSIS

- Recommended method: Airborne particles collected on a sorbent cartridge containing polyurethane foam; analyte deposited on the cartridge extracted with 5% diethyl ether in hexane; extract analyzed by GC-ECD; recommended air flow 5 L/min; sample volume 1000 L.

REFERENCE

Alltech Corporation. 1995. *Product Catalog and Literature*, Deerfield, IL.

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92 Diethyl Ether

Synonyms: ethyl ether, solvent ether, diethyl oxide; formula $(C_2H_5)_2O$; structure: $H_3C–CH_2–O–CH_2–CH_3$; MW 74.14; CAS [60-29-7]; used as a solvent; used in organic synthesis and as an anesthetic; colorless liquid; pungent odor; sweet burning taste; boils at 34.6°C; vapor pressure 439 Torr at 20°C; freezes at −116°C; density 0.71 g/mL at 20°C; miscible with organic solvents; solubility in water 6 g/100 mL; forms azeotrope with water (1.3%); extremely flammable; narcotic.

ANALYSIS OF AQUEOUS SAMPLES

- Analyte purged out from the sample matrix by the purge and trap extraction method; desorbed from the sorbent trap by heating and backflushing with He; transferred into a capillary GC column interfaced to a mass spectrometer; identified by mass spectra and retention time (U.S. EPA Method 524.2, 1995).
  - GC column: a fused silica capillary column such as VOCOL, DB-5, DB-624, or equivalent.
  - Characteristic masses for GC/MS identification: 74 (primary ion), 59, 45, and 73.
  - Detection level: in the range of 0.1 mg/L.
- Aqueous samples directly injected onto an appropriate GC column for FID detection.
  - Poor detection level and the sensitivity is much lower than the purge and trap method.

AIR ANALYSIS

- Air drawn through a solid sorbent tube containing coconut shell charcoal (100 mg/50 mg); diethyl ether desorbed with 1 mL ethyl acetate (30 min contact time) and analyzed by GC-FID (NIOSH Method 1610, 1985); recommended flow rate 0.1 L/min; sample volume 1 L.
  - GC column: stainless steel packed with Porapak Q (50/80 mesh). Use a capillary column to prevent coelution of CS_2, hexane, and low molecular weight ketones.
  - Working range: 100–2700 mg/m^3 for a 3 L air sample.

    (1 ppm diethyl ether = 3.03 mg/m^3 at NTP)

REFERENCES

National Institute for Occupational Safety and Health. 1985. *NIOSH Manual of Analytical Methods*, 3rd edition and updates, Cincinnati, OH: National Institute for Occupational Safety and Health.

US EPA. 1995. *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry.* Cincinnati, OH: Office of Research and Development.

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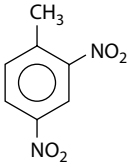
93 2,4-Dinitrotoluene

Formula: $C_7H_6O_4N_2$; MW 182.14; structure:



CAS [121-14-2]; crystalline solid; melts between 67°C and 70°C; insoluble in water; soluble in organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples repeatedly extracted with methylene chloride; extracts combined and concentrated by evaporation of methylene chloride solvent exchanged to hexane; Florisil cleanup (for removal of interferences); extract analyzed on GC-ECD or GC/MS.
- Soil, sediment, or solid waste extracted with methylene chloride by sonication or Soxhlet extraction; extract concentrated; exchanged to hexane (if Florisil cleanup required), analyzed by GC-ECD or GC/MS.
  - For Florisil cleanup, column eluted with methylene chloride/hexane (1:9) and then with acetone/methylene chloride (1:9) mixture; analyte eluted into the latter fraction.
  - Column packed: 1.95% QF-1/1.5% OV-17 on Gas-Chrom Q (80/100 mesh) or 3% SP-2100 on Supelcoport (100/120 mesh) or equivalent; fused silica capillary column, such as PTE-5, SPB-5, DB-5, Rtx-5, or equivalent.
  - 2,6-Isomer elutes before the 2,4-isomer.
  - Characteristic masses for GC/MS identification: 165, 63, and 182 (electron impact ionization); 183, 211, and 223 (chemical ionization).
  - Suggested surrogate/IS: aniline d5, 4-fluoroaniline, nitrobenzene d5, and 1-fluoronaphthalene.
  - Detection level: in the range of 0.02 mg/L may be achieved when determined by GC-ECD (for aqueous samples concentrated by 1000 times).
  - Samples collected in glass containers, refrigerated, extracted within 7 days of collection, and analyzed within 40 days of extraction.

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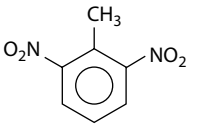
94 2,6-Dinitrotoluene

Formula: $C_7H_6O_4N_2$; MW 182.14; structure:



CAS [606-20-2]; crystalline solid; melts ≈5°C; insoluble in water; soluble in most organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted with methylene chloride; extract concentrated and solvent exchanged to hexane; Florisil cleanup (for removal of interferences), extract analyzed on GC-ECD or GC/MS.
- Soil, sediment, or solid waste extracted with methylene chloride by sonication or Soxhlet extraction: extract concentrated; exchanged to hexane (if Florisil cleanup required), analyzed by GC-ECD or GC/MS.
  - For Florisil cleanup, column eluted with methylene chloride/hexane (1:9) and then with acetone/methylene chloride (1:9) mixture; analyte eluted into the latter fraction.
  - Column-packed: 1.95% QF-1/1.5% OV-17 on Gas-Chrom Q (80/100 mesh) or 3% SP-2100 on Supelcoport (100/120 mesh) or equivalent, capillary: fused silica capillary column, such as PTE-5, SPB-5, DB-5, Rtx-5, or equivalent.
  - 2,6-isomer elutes before the 2,4-isomer.
  - Characteristic masses for GC/MS identification: 165, 89, and 121 (electron impact ionization); 183, 211, and 223 (chemical ionization).
  - Suggested surrogate/IS: aniline d5, 4-fluoroaniline, nitrobenzene d5, and 1-fluoronaphthalene.
  - A detection level: in the range of 0.02 mg/L may be achieved for aqueous samples concentrated up by 1000 times and determined by GC-ECD.
  - Samples collected in glass containers, refrigerated, extracted within 7 days of collection, and analyzed within 40 days of extraction.

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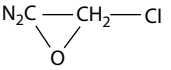
95 Epichlorohydrin

Synonyms: l,2-epoxy-3-chloropropane; 2-(chloromethyl)oxirane; 2,3-epoxy-propyl chloride; formula: C_3H_5ClO; structure:



MW 92.53; CAS [106-89-8]; used to make epoxy resins, adhesives, surfactants, and plasticizers, and also as a solvent for gums, resins, and paints; colorless liquid; chloroform-like odor; boils at 116°C; solidifies at −57°C; vapor pressure 12 Torr at 20°C; density 1.18 g/mL at 20°C; moderately soluble in water (6.6% at 20°C), soluble in most organic solvents; moderately toxic, carcinogenic, and a strong irritant (Patnaik, 2007).

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples subjected to the purge and trap concentration method; analyte thermally desorbed from the trap and swept onto a GC column for separation from other volatile substances and detection by HECD, ECD, or a mass spectrometer.
  - Purging efficiency low because of its moderate solubility.
  - Purging efficiency may be enhanced by heating the purging vessel.
  - Analyte unstable; polymerizes in presence of acids, alkalies, and catalysts.
  - Characteristic masses for GC/MS identification: 57, 27, 29, and 31; peak ratios: 57:27:29:31 = 100:96:71:39.
  - Samples collected in glass vials without headspace, refrigerated, and analyzed within 14 days.

AIR ANALYSIS

- Adsorbed over coconut shell charcoal (100 mg/50 mg); desorption with CS_2; epichlorohydrin desorbed into CS_2 then determined by GC-FID (NIOSH Method 1010, 1984); recommended flow rate 100 mL/min; sample volume 20 L.
  - GC column: Chromosorb 101 or equivalent.

  (1 ppm epichlorohydrin in air = ∼3.78 mg/m^3 at NTP)

REFERENCE

Patnaik, P. 2007. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 3rd edn. New York: John Wiley and Sons.

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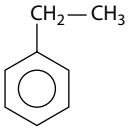
96 Ethylbenzene

Synonym: phenylethane; formula C_8H_{10}; structure:



MW 106.18; CAS [100-41-4]; used as a solvent and an intermediate to produce styrene monomer; colorless liquid; characteristic aromatic odor; boils at 136°C; vapor pressure 7.1 Torr at 21°C; freezes at −95°C; density 0.86 g/mL at 20°C; solubility in water 0.015 g/100 g; readily miscible with organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Purge and trap method; ethylbenzene transferred from aqueous to vapor phase under helium purge; analyte adsorbed on a sorbent trap; thermally desorbed out from the sorbent trap backflushed with He onto a GC column for separation from other volatile compounds; determined by PID, FID, or a mass spectrometer.
- Solid samples mixed with methanol; a portion of methanol extract spiked into a measured volume of water (25 mL) in the purging vessel; subjected to purge and trap concentration and analyzed as above.
- Alternatively, ethylbenzene thermally desorbed from the solid sample under He purge (without any solvent treatment) onto the GC column and analyzed on a suitable detector or by a mass spectrometer as above.
  - Characteristic masses for GC/MS identification: 106 and 91.
  - Limit of detection: in the range 0.5 mg/L for a 5 mL sample volume, when detected by PID.
  - GC column: a nonpolar fused silica capillary column, such as DB-5, SPB-5, VOCOL, DB-624, or equivalent; packed column: 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent.
  - Recommended surrogate/IS: ethylbenzene-d_5 (*m/z* 111) and 1,4-difluorobenzene (*m/z* 114, 63, 88).
  - Samples collected in glass containers without headspace, refrigerated, and analyzed within 7 days. Samples preserved with 1:1 HCl (0.2 mL acid/40 mL sample) may be analyzed in 14 days.

AIR ANALYSIS

- Air drawn through a sorbent tube packed with coconut shell charcoal (100 mg/50 mg); analyte desorbed into CS_2 (more than 30 min standing); CS_2 extract analyzed by GC-FID (NIOSH Method 1501, 1984); recommended air flow rate 100 mL/min; sample volume 20 L. **Q1**
  - GC column: packed column 10% OV-275 on 100/120 mesh Chromosorb W-AW, Porapak P (50/80 mesh), or equivalent.
- Alternatively, air collected in a SUMMA passivated stainless steel canister, either by pressurizing the canister using a sample pump or by preevacuating. The canister is then

connected to an analytical system; air transferred to a cryogenically cooled trap; cryogen removed and temperature raised; analyte revolatilized; separated on a GC column; determined by PID, FID, or a mass spectrometer (U.S. EPA Method TO-14, 1988).

- Alternatively, air drawn through a cartridge packed with either Tenax (1 g) or carbon molecular sieve (0.5 g); cartridge heated at 350°C under the helium purge. The analyte is transported to the front of a precooled GC column, temperature programmed; ethylbenzene determined on a PID, FID, or a mass spectrometer; recommended air flow rate 0.5 L/min; sample volume 50 L.
  - No precision and accuracy data available for this method.

(1 ppm ethylbenzene in air = 4.34 mg/m^3 at NTP)

REFERENCES

National Institute for Occupational Safety and Health. 1984. *NIOSH Manual of Analytical Methods*, 3rd edn. Cincinnati, OH: National Institute for Occupational Safety and Health.

US EPA. 1988. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Supplement*. Research Triangle Park, NC: Atmospheric Research and Exposure Assessment Laboratory.

97 Ethyl Chloride

Synonym: chloroethane; formula: C_2H_5Cl; MW 64.52; CAS [75-00-3]; colorless gas at room temperature with ether-like odor; liquefies at 12.5°C, slightly soluble in water, miscible with organic solvents.

ANALYSIS OF AQUEOUS SAMPLES

- Aqueous samples subjected to the purge and trap extraction method; volatile analyte thermally desorbed out from the trap on heating and swept onto a GC column for separation; detected by HECD, ECD, or MDS; low retention time.
  - Characteristic masses for GC/MS identification: 64 and 66.
  - Limit of detection: in the range 0.1 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: bromochloromethane and 1,2-dichloro-ethane-d_4.
  - Samples collected in glass/plastic containers without headspace, refrigerated, and analyzed within 14 days.

See Chapter 27 for GC columns and conditions and a detailed discussion.

AIR ANALYSIS

The following methods are recommended:

- Adsorbed over carbon molecular sieve (~400 mg); desorbed at 350°C into a cryogenically cooled trap; flash evaporated onto a capillary column GC/MS system; recommended sample volume 10 L; flow rate 100 mL/min.
- Collected in a SUMMA passivated canister or liquid argon trap; transferred onto a precooled GC column; determined by ECD or MSD.
- The precision and accuracy of the above methods for this compound are not established.

(1 ppm ethyl chloride in air = ~2.2 mg/m^3 at NTP)

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98 Ethylene Chlorohydrin

Synonyms: 2-chloroethanol, 2-chloroethyl alcohol; formula: C_2H_5OCl; structure: $Cl–CH_2–CH_2–OH$; MW 80.52; CAS [107-07-3]; used as a solvent for cellulose esters and in making ethylene glycol and ethylene oxide; colorless liquid with a faint ether odor; boils at 129°C; freezes at −67°C; density 1.197 g/mL at 20°C; soluble in water, alcohol, and ether; highly toxic.

ANALYSIS OF AQUEOUS SAMPLE

- Purge and trap concentration; sample purged with He under heating; analyte desorbed from the trap by heating and backflushing with He; transferred onto a GC column for separation; determined by GC-FID or a mass spectrometer.
  - No precision and accuracy data are available.
  - Purging efficiency is low because of high solubility of the analyte in water. Purging vessel should be heated under the He purge.

AIR ANALYSIS

- Air drawn through a solid sorbent tube containing petroleum charcoal (100 mg/50 mg); analyte desorbed with 1 mL 5% 2-propanol in CS_2 (more than 30 min standing) and analyzed by GC-FID (NIOSH Method 2513, 1985); recommended flow rate 0.1 L/min; sample volume 20 L.
  - GC column: 10% FFAP on 80/100 mesh Chromosorb WHP or equivalent.
  - Working range: 0.5–15 ppm for a 20 L air sample.

    (1 ppm ethylene chlorohydrin in air = 3.29 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Safety and Health. 1985. *NIOSH Manual of Analytical Methods*, 3rd edition and update. Cincinnati, OH: National Institute for Occupational Safety and Health.

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99 Ethylene Dibromide

Synonyms: 1,2-dibromoethane, EDB; formula: $BrCH_2CH_2Br$; MW 187.88; CAS [106-93-4]; used in fumigant and antiknock gasolines; colorless heavy liquid; chloroform odor; boils at 131°C; freezes at 10°C; vapor pressure 11 Torr at 20°C; density 2.7 g/mL at 25°C; slightly soluble in water (0.4%); miscible with alcohol and ether; irritant and toxic.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Purge and trap method; aqueous samples purged with He; EDB thermally desorbed from the sorbent trap and swept by an inert gas onto a GC column for separation from other volatile compounds; analyzed by a halogen-specific detector or a mass spectrometer.
- Solid samples mixed with methanol; methanol extract spiked into water; aqueous solution subjected to purge and trap extraction and analyzed as above.
  - Characteristic masses for GC/MS identification: 107, 109, and 188.
  - GC column: a fused silica capillary column such as DB-5, SPB-5, Rtx-5, or equivalent.
  - Limit of detection: the range 0.1 μg/L for a 5 mL sample aliquot purged.
  - Samples collected in glass containers without headspace, refrigerated, and analyzed within 7 days.

AIR ANALYSIS

- Air drawn through a sorbent tube containing coconut shell charcoal (100 mg/50 mg); EDB desorbed from the charcoal by treatment with 10 mL 99:1 benzene–methanol (allowed to stand for 1 h); the solvent extract analyzed by GC-ECD (NIOSH Method 1008, 1987); recommended flow rate 100 mL/min; sample volume 10 L.
  - GC column: 3% OV 210 on Gas Chrom Q (80/100 mesh).
  - IS: 1,2-dibromopropane or 1,1,2,2-tetrachloroethane.
- Air collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; sample transferred into a cryogenically cooled trap attached to a GC column; the trap heated; EDB separated on the GC column and determined by a mass spectrometer (U.S. EPA Method TO-14).

  (1 ppm EDB in air = 7.68 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Health and Safety. 1987. *NIOSH Manual of Analytical Methods*, 3rd edition and update. Cincinnati, OH: National Institute for Occupational Health and Safety.

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100 Ethylene Glycol

Synonym: 1,2-ethanediol; formula: $HOCH_2CH_2OH$; MW 62.07; CAS [107-21-1]; used as antifreeze in cooling and heating systems and in hydraulic brake fluids; colorless liquid; sweet taste; hygroscopic; density 1.11 g/mL; boils at 197.5°C; freezes at −13°C; highly soluble in water, lower alcohols, acetone, and pyridine; toxic.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES (SUGGESTED METHOD)

- Aqueous samples directly injected onto a GC column and determined by an FID.
  - GC column: a polar column (polar PEG-type phase), such as Supelcowax 10, Nukol, or equivalent.
  - No precision or accuracy data are available.
- 10 g soil, sediment, or solid wastes sonicated with 50 mL 2% isopropanol in water; extract injected onto GC column; determined on FID.
  - No precision or accuracy data are available.
  - Detection level: in the range 50 mg/kg.

AIR ANALYSIS

- Air drawn through a glass fiber filter and then through a sorbent tube containing silica gel (520 mg/260 mg), ethylene glycol desorbed out from silica gel with 2% isopropanol in water (on 5 min standing); the analyte in eluant determined by GC-FID (NIOSH Method 5500, 1984); recommended air flow rate 0.2 L/min; sample volume 30 L.
  - GC column: packed glass column 3% Carbowax 20 M on 80/100 mesh Chromosorb 101. Any appropriate polar column may be used.
  - The working range for a 3 L air sample was found to be 7–330 mg/m^3.
- Alternatively, air bubbled through water; aqueous solution of the analyte oxidized with periodic acid into formaldehyde; the latter analyzed by chromotropic acid colorimetric method (Tucker and Deye, 1981).
- Also the air may be sampled using the adsorbents porous polymer Amberlite XAD-2 and –XAD-7. Ethylene glycol and its glycol ether derivatives are desorbed with diethyl ether and analyzed by GC (Andersson et al. 1982).

(1 ppm ethylene glycol in air = 2.54 mg/m^3 at NTP)

REFERENCES

Andersson, K., Levin, J.O., Lindahl, R., and C.A. Nilsson. 1982. Sampling of ethylene glycol and ethylene glycol derivatives in work-room air using Amberlite XAD, *Chemosphere*, 11: 1115–1119.

National Institute for Occupational Safety and Health. 1984. *NIOSH Manual of Analytical Chemistry,* 3rd edn. Cincinnati, OH*:* National Institute for Occupational Safety and Health.

Tucker, S.P. and G.J. Deye. 1981. A Sampling and analytical method for ethylene glycol in air. *Anal. Lett.,* 14(12): 959–976.

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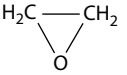
101 Ethylene Oxide

Synonyms: 1,2-epoxyethane, oxirane; formula: C_2H_4O; structure:



MW 44.06; unstable, ring cleaves readily; CAS [75-21-8]; used as a fumigant and sterilizing agent, and in the manufacture of many glycol ethers and ethanolamines; colorless gas with ether-like odor; liquefies at 10.4°C; density 0.88 g/mL at 10°C; vapor pressure 1095 Torr at 20°C; soluble in water and most organic solvents; highly flammable, toxic, and severe irritant.

AIR ANALYSIS

- Air drawn through a solid sorbent tube containing HBr-coated petroleum charcoal; bromo derivative of analyte formed desorbed with dimethylformamide (DMF) and analyzed by GC-ECD (NIOSH Method 1614, 1987); recommended air flow 100 mL/min; sample volume 10 L.
  - Calibration standard solutions: 2-bromoethanol in DMF.
  - GC column: 10% SP-1000 on Chromosorb WHP or equivalent.
- Alternatively, air bubbled through impingers contain 0.1 N H_2SO_4; ethylene oxide converted into ethylene glycol; latter measured by GC-FID (Romano and Renner, 1979).
  - Activated charcoal impregnated with H_2SO_4 may alternatively be employed in air sampling; glycol formed desorbed with water or a suitable organic solvent analyzed by GC-FID.
- Ethylene oxide in air may be measured directly *in situ* by a rapid colorimetric technique (Pritts et al., 1982). Air is drawn through a multipart detector tube consisting of three reactor tubes: containing periodic acid, xylene, and conc. H_2SO_4, respectively. Ethylene oxide is oxidized by periodic acid to formaldehyde that then reacts with xylenes to form diaryl methylene compounds. The latter products are oxidized by H_2SO_4, impregnated on silica gel to red *p*-quinoidal compounds. Thus, the color in the detector tube changes from white to reddish brown and the concentration of the analyte in the range 5–1000 ppm may be monitored from the length of stain formed in the detector tube.

  (1 ppm ethylene oxide in air = 1.80 mg/m^3 at NTP)

REFERENCES

Romano, S. and V.A. Renner. 1979. Analysis of ethylene oxide—Worker exposure. *Am. Ind. Hyg. Assoc. J.*, 40: 742–745.

Pritts, I.M., McConnaughey, P.W., Roberts, C.C., and E.S. McKee. 1982. Ethylene oxide detection and protection. In *The Toxic Materials in the Atmosphere: Sampling and Analysis*, ASTM Special Technical Publication, vol. 786. Philadelphia, PA: American Society for Testing and Materials, p. 14.

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102 Formaldehyde

Synonyms: methanal, methylene oxide, oxymethane; formula: HCHO; MW 30.03; CAS [50-00-0]; constitutes about 50% of all aldehydes present in air; released in trace quantities from pressed wood products, burning wood, and synthetic polymers; and automobiles; colorless gas at ambient conditions; pungent suffocating odor; liquefies at −19.5°C; solidifies at −92°C; density 1.07 (air = 1); very soluble in water, soluble in organic solvents; readily polymerizes; flammable, toxic, and carcinogenic (Patnaik, 2007).

WATER ANALYSIS

Aqueous samples analyzed by HPLC using a post column reaction detector; formaldehyde separated on a reversed phase C-18 column; derivatized with 3-methyl-2-benzothiazolinone hydrazone and detected at 640 nm (Igawa et al., 1989). (The method was developed for cloud and fogwater analysis.)

AIR ANALYSIS

- Formaldehyde may be analyzed by several techniques involving GC, colorimetry, polarography, HPLC, and GC/MS.
- Air drawn through a solid sorbent tube containing 10% (2-hydroxymethyl) piperidine on XAD-2 (120 mg/60 mg); oxazolidine derivative of formaldehyde formed desorbed into toluene under ultrasonic conditions (60 min); analyzed by GC-HD (NIOSH Method 2541, 1989); recommended air flow 200 mL/min; sample volume 15 L.
  - Calibration standards prepared from formaldehyde (formalin) stock solutions; each standard injected into 120 mg portions coated-adsorbent; derivative desorbed into toluene and analyzed by GC-FID as above; calibration curve constructed (plotting area/height response against concentrations) for quantitation.
  - GC column: fused silica capillary column such as DBWax or equivalent.
- Alternatively, air passed through a solid sorbent tube containing 2-(benzylamino)ethanol on Chromosorb 102 or XAD-2; the derivative, 2-benzyloxazolidine desorbed with isooctane and analyzed by GC-FID (NIOSH Method 2502, 1984).
  - 2-Benzyloxazolidine peak often masked under interferences from decomposition and/or polymerization products from derivatizing agent; isooctane solution may be readily analyzed by GC/MS using a DB-5 capillary column.
- Alternatively, air drawn through a PTFE membrane followed by sodium bisulfite solution in impingers; impinger solution treated with chromotropic acid and H_2SO_4; color developed due to formation of a derivative of formaldehyde; absorbance measured by a spectrophotometer at 580 nm; a standard calibration curve prepared from formaldehyde standard solutions for quantitation (NIOSH Method 3500, 1989); recommended air flow 500 mL/min; sample volume 50 L.
  - Phenols, alcohols, olefins, and aromatics interfere in the test to a small extent.
- Air drawn through a midget bubbler containing 15 mL Girard T reagent; Girard T derivative of formaldehyde analyzed by polarography; a calibration curve constructed (plotting concentration formaldehyde/15 mL Girard T solution vs. diffusion current) for quantitation (NIOSH Method 3501, 1989); recommended air flow rate 100 mL/min; sample volume 10 L.
  - The half-wave potential for the derivative versus saturated calomel electrode is −0.99 V.

- Alternatively, air drawn through Florisil or silica gel adsorbent coated with acidified 2,4-DNPH; the DNPH derivative of formaldehyde desorbed with isooctane, and solvent exchanged to methanol or acetonitrile; the solution analyzed by reverse phase HPLC (U.S. EPA Method TO-11, 1988); recommended air flow rate 500 mL/min; sample volume 100 L.
  - Formaldehyde and several other low molecular weight aldehydes and ketones containing 1 to 7 C atoms can also be determined by the modified method, US EPA To 11A (US EPA, 1999). A known volume of ambient air is drawn through a pre-packed cartridge coated with acidified DNPH. The DNPH -formaldehyde derivatives eluted with acetonitrile and determined by isocratic reversed-phase HPLC using an UV detector at 360 nm. Air flow rate is recommended as 100 mL to 2 L/min depending on the carbonyl concentration in the test atmosphere.
- Alternatively, a measured volume of air drawn through an impinger containing ammonium acetate and 2,4-pentanedione; formaldehyde forms a fluorescence derivative, 3,5-diacety l-l,4-dihydrolutidine; fluorescence of the solution measured by a filter fluorometer (Dong and Dasgupta, 1987).

(1 ppm formaldehyde in air = 1.23 mg/m^3 at NTP)

REFERENCES

Dong, S. and P.K. Dasgupta. 1987. Fast fluorometric injection analysis of formaldehyde in atmospheric water, *Environ. Sci. Technol*., 21(6): 581.

Igawa, M., Munger, W.J., and M.R. Hoffmann. 1989. Analysis of aldehydes in clouds- and fog water samples by HPLC with a post-column reaction detector, *Environ. Sci. Technol*., 23(5): 556.

National Institute for Occupational Safety and Health. 1984–1989. *NIOSH Manual of Analytical Methods*, 3rd edition and updates. Cincinnati, OH: National Institute for Occupational Safety and Health.

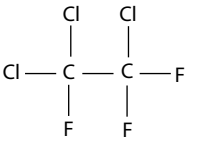
Patnaik, P. 2007. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 3rd edn. New York: John Wiley and Sons.

US EPA. 1988. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.* Cincinnati, OH: Office of Research and Development.

US EPA. 1999. *Method TO 11A, Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC), Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.* Research Triangle Park, NC: Atmospheric Research and Exposure Assessment Laboratory.

103 Freon 113

Synonyms: 1,1,2-trichloro-1,2,2-trifluoroethane, fluorocarbon-113; formula $C_2O_3F_3$; structure:



MW [37.37]; CAS [76-13-1]; colorless liquid with a characteristic odor; boils at 47.6°C; freezes at −35°C; vapor pressure 284 Torr at 20°C; density 1.56 g/mL; insoluble in water; miscible with organic solvents; used as a refrigerant and dry cleaning solvent, and also for extracting oil, grease, and hydrocarbons in chemical analysis.

ANALYSIS OF AQUEOUS SAMPLES

- An aliquot of sample is purged with He; the analyte adsorbed over a trap (Tenax or equivalent); the trap heated under He flow; the analyte desorbed from the trap and transported onto a GC column for separation from other volatile compounds and determination by a halogen-specific detector (ECD or HECD) or a mass spectrometer.
  - The characteristic ions for GC/MS identifications 101, 151, 103, 153, 85, and 66.
  - Samples collected in glass containers without headspace, refrigerated, and analyzed within 14 days of collection.

AIR ANALYSIS

- Air drawn through coconut shell charcoal (100 mg/50 mg); analyte desorbed into CS_2 (allowed to stand for 30 min) and analyzed by GC-FID (NIOSH Method 1020, 1994); flow rate 10–50 mL/min; sample volume 1–2 L.
- Air collected in a cryogenic trap under liquid argon; trap warmed; sample transferred onto a precooled GC column; temperature programmed; separated on the column and determined by FID, halogen-specific detector, or GC/MS.

(1 ppm freon-113 in air = 7.66 mg/m^3 at NTP)

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104 Hydrogen Cyanide

Formula: HCN; MW 27.03; CAS [74-90-8]; occurs in the root of certain plants, beet sugar residues, coke oven gas, and tobacco smoke; released during combustion of wool, polyurethane foam, and nylon; produced when metal cyanides react with dilute mineral acids; colorless or pale liquid or a gas; odor of bitter almonds; boils at 25.6°C; solidifies at −13.4°C; density of liquid 0.69 g/mL at 20°C and gas 0.95 (air = 1) at 31°C; soluble in water and alcohol, very weakly acidic; dangerously toxic and highly flammable (Patnaik, 2007).

ANALYSIS OF AQUEOUS SAMPLES

- Aqueous samples distilled directly without any acid treatment; HCN liberated and collected in NaOH solution; cyanide analyzed by colorimetric or by ion selective electrode method (see Chapter 19).
- Avoid acid treatment of samples, as it converts metal cyanides into HCN.
- Test papers treated with *p*-nitrobenzaldehyde and K_2CO_3 produces reddish-purple stain due to HCN.
- Method suitable for detecting 10 ppm HCN.
- The presence of HCN indicated by color change of 4-(2-pyridylazo) resorcinol–palladium in carbonate–bicarbonate buffer solution from intense red to yellow (Carducci et al., 1972).
- The method originally developed for determination of plants, tissue, and toxicological substances. No precision and accuracy data are available for environmental samples of aqueous matrices.

AIR ANALYSIS

- Air drawn through a solid sorbent tube containing soda lime (600 mg/200 mg); cyanide complex desorbed into deionized water; solution treated with *N*-chlorosuccinimide–succinimide oxidizing reagent; after several minutes standing barbituric acid–pyridine coupling reagent added; color development measured at 580 nm by a spectrophotometer; concentration determined from a calibration standard (NIOSH Method 6010, 1994); recommended flow rate 100 mL/min; sample volume 50 L.
  - Oxidizing agent: to 10 g succinimide in 200 mL water, add 1 g *N*-chlorosuccinimide; stirred to dissolve; volume adjusted to 1 L; stable for 6 months if refrigerated.
  - Coupling agent: to 6 g barbituric acid in 30 mL water, add 30 mL pyridine slowly with stirring; adjust volume to 100 mL; stable for 2 months if refrigerated.
- Alternatively, 50 L air bubbled through 10 mL 0.1 N KOH solution at a rate of 0.5 L/min; the solution analyzed for CN^- by ion-selective electrode method (NIOSH Method 7904, 1994).

$$\text{HCN} = \frac{(W_b - B_b) \times 1.04}{V} \text{ mg/m}^3$$

where

W_b and B_b are μg CN^- in sample bubbler and media blank bubbler, respectively
V is the air volume (L) sampled (and HCN to CN^- stoichiometric factor 1.04)

  - Metals interfere in the test, forming strong complexes with CN^-; such interference is eliminated by special treatment with EDTA.
- Alternatively, air bubbled through an impinger containing 15 mL 0.2 N NaOH solution; HCN converted into NaCN; content of impinger transferred into a vial, rinsed with 2 mL 0.2 N NaOH (total volume 17 mL); sealed and heated overnight in an oven; NaCN hydrolyzed into sodium formate; contents cooled and diluted to 50 mL; formate ion analyzed by ion chromatography (Dolzine et al., 1982).
  - Concentration of formate determined from a formate calibration standards in 0.068 N NaOH.
  - μg HCN in sample = μg/mL formate ion $\times$ 0.60 $\times$ 50 (factor for converting formate ion to HCN 0.60, sample solution 50 mL).
  - mg HCN/m^3 air = μg HCN in sample/liters of air sampled.
  - Separator column: strong base anion-exchange resin; suppressor column: strong acid-resin in hydrogen form; eluting solvent 0.005 M sodium borate.

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Carducci, C.N., Luis, P., and A. Mascaro. 1972. *Microchim. Acta*, 3: 339–344.

Dolzine, T.W., Esposito, G.G., and D.D. Rinehart. 1982. Determination of hydrogen cyanide in air by ion chromatography. In *Toxic Materials in the Atmosphere, ASTM Special Technical Publication*, vol. 786. Philadelphia, PA: American Society for Testing and Materials, p. 142.

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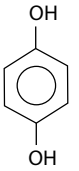
Patnaik, P. 2007. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 3rd edn. New York: John Wiley and Sons.

105 Hydroquinone

Synonyms: 1,4-benzenediol, hydroquinol, *p*-dihydroxybenzene; formula: $C_6H_6O_2$; structure:



MW 110.11; CAS [123-31-9]; crystalline solid; melts at 170°C; boils at 286°C; low solubility in water (7%); dissolves readily in alcohol and ether; oxidizes slowly in air.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples serially extracted with methylene chloride; the extract concentrated and analyzed by GC/MS.
  - The characteristic masses for GC/MS identification: 110 (primary ion), 81, 53, and 55.
  - GC column: a fused silica capillary column, such as DB-5 or equivalent.
- Soil, sediments, and solid waste mixed with anhydrous Na_2SO_4; sonicated or Soxhlet extracted with methylene chloride; extract concentrated and analyzed by GC/MS.

AIR ANALYSIS

- A measured volume of air is drawn through a 0.8 mm cellulose ester membrane filter; the particulates of hydroquinone extracted with 1% acetic acid in water; extract analyzed by HPLC using an UV detector at 290 nm (NIOSH Method 5004, 1984); recommended air flow rate 2 L/min; sample volume 100 L.
  - HPLC column: M-Bondapak C-18 or equivalent (e.g., 25 cm × 4.6 mm ID Partisil 10-ODS) at ambient temperature, 400–600 psi; mobile phase 1% acetic acid in water, 1 mL/min; calibration standard: same as above.
  - Sample stable for 2 weeks at ambient temperature.
  - Acetic acid stabilizes the sample, preventing air oxidation.
  - Working range is 0.5–10 mg/m^3 for a 100 L air sample.
  - Hydroquinone could occur in air at ambient temperature as particulates and not vapor, as its vapor pressure is too low.

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National Institute for Occupational Safety and Health. 1984. *NIOSH Manual of Analytical Methods*, 3rd edn. Cincinnati, OH: National Institute for Occupational Safety and Health.

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106 Hydrogen Sulfide

Formula: H_2S; MW 34.08; CAS [7783-06-4]; occurs in natural gas and sewer gas; formed when metal sulfides react with dilute mineral acids; colorless gas with rotten egg odor; liquefies at −60.2°C; solidifies at 85.5°C; slightly soluble in water (4000 mg/L at 20°C); aqueous solution unstable, absorbs oxygen and decomposes to sulfur; highly toxic and flammable.

AIR ANALYSIS

- Commercially available photorateometric analyzers may perform atmospheric monitoring of H_2S.
  - Paper tape H_2S analyzers use paper strips treated with lead acetate; colored stains of PbS detected by photocells (Kimbell, 1982); color ranges from light yellow to silvery black; extremely high signal amplification required to measure stains far too light in color for rapid and continuous measurement of H_2S at low ppb level.
- H_2S exposure may be monitored by diffusion type colorimetric dosimeters (such as Vapor Gard); color changes from white to brown–black; dosage exposure measured from the length of stain in the indicator tube.
  - Hydrogen sulfide in the air may also be measured by the NIOSH Method 6013 (NIOSH, 1994). A measured volume of air is sampled using adsorbent tubes packed with coconut charcoal, and desorbed with ammonium hydroxide (NH_4OH) and hydrogen peroxide (H_2O_2). H_2S is converted into sulfate which is analyzed by ion chromatography. There may be positive interference, however, from the presence of sulfur dioxide in the air.
  - Also, H_2S in ambient air may be measured by the OSHA Method 1008 (OSHA, 2006). Between 5 and 12 L of air at a flow rate of 50–500 mL/min is drawn through silver nitrate ($AgNO_3$)-coated silica gel. H_2S reacts with silver to form silver sulfide (Ag_2S), which is then extracted with an aqueous solution of sodium cyanide/sodium hydroxide (NaCN/NaOH) mixture, followed by treatment with H_2O_2 to convert into sulfate. The sulfate anion is measured by ion chromatography using a conductivity detector.

(1 ppm H_2S in air = 1.39 mg/m^3 at NTP)

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Kimbell, C.L. 1982. Atmospheric monitoring for hydrogen sulfide by photometric analysis. In *Toxic Materials in the Atmosphere: Sampling and Analysis*, ASTM Special Technical Publication vol. 786. Philadelphia, PA: American Society for Testing and Materials, p. 60.

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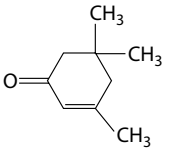
107 Isophorone

Synonyms: 1,1,3-trimethyl-3-cyclohexene-5-one, isoacetophorone; formula: $C_9H_{14}O$; structure:



MW 138.20; CAS [78-59-1]; used as a solvent for vinyl resins and cellulose esters; boils at 215°C; solidifies at −8°C; density 0.92 g/mL at 20°C; slightly soluble in water; readily miscible with alcohol, ether, and acetone.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted with methylene chloride; extract concentrated and solvent exchanged to hexane; Florisil cleanup (for removal of interferences); extract analyzed on GC-FID or GC/MS.
- Soil, sediments, or solid waste extracted with methylene chloride by sonication or Soxhlet extraction; extract concentrated; exchanged to hexane (if Florisil cleanup required); analyzed by GC-FID or GC/MS.
  - For Florisil cleanup, column eluted with methylene chloride/hexane (1:9) and then with acetone/methylene chloride (1:9) mixture; analyte eluted into the latter fraction.
  - Column-packed: 1.95% QF-1/1.5% OV-17 on Gas-Chrom Q (80/100 mesh) or 3% SP-2100 on Supelcoport (100/120 mesh) or equivalent; capillary: fused silica capillary column, such as PTE-5, SPB-5, DB-5, Rtx-5, or equivalent.
  - Characteristic masses for GC/MS identification: 82, 95, and 138.
  - Suggested surrogate/IS: aniline d_5, 4-fluoroaniline, nitrobenzene d_5, and 1-fluoronaphthalene.
  - Samples collected in glass containers, refrigerated, extracted within 7 days of collection, and analyzed within 40 days of extraction.

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108 Methane

Synonym: marsh gas; formula: CH_4; MW 16.04; CAS [74-82-8]; prime constituent of natural gas; formed from petroleum cracking, decay of animal and plant remains, and anaerobic fermentation of municipality landfill contents; occurs in marshy pools, landfill gas, and leachate from the landfill; colorless and odorless gas; lighter than air; gas density 0.717 g/L; liquefies at −61.4°C; soluble in organic solvents, slightly soluble in water (25 mg/L); flammable gas.

ANALYSIS OF AQUEOUS SAMPLES AND SLUDGE DIGESTER GAS

Samples from wells are collected using a sufficiently submerged pump. Sludge digester gas samples are collected in sealed containers, such as glass sampling bulbs with three-way stopcocks. The containers are flushed with the digester gas or the gases from the aqueous samples to purge out air from the containers, prior to sample collection. Analytical methodologies are similar for both the aqueous and the sludge-digester gas samples. Gas chromatography method, discussed in Chapter 12 is also applicable.

- A measured volume of sample transferred into an Orsat-type gas-analysis apparatus; sample equilibrated to atmospheric pressure by adjusting the leveling bulb. CO_2 removed from the sample by passing through KOH solution. O_2 removed by passing through alkaline pyrogallol. H_2 removed by passing over heated CuO. CH_4 in the sample then oxidized to CO_2 and H_2O by passing through a catalytic oxidation assembly or a slow combustion pipet assembly by controlled electrical heating using a platinum filament. Volume of CO_2 formed during combustion determined to measure the fraction of methane originally present.
- Methane in the aqueous sample is determined by commercially available direct-readout combustible gas detector.
- The method determines the partial pressure of methane in the gas phase above the solution (Henry's law). Methane catalytically oxidizes on a heated platinum filament that is part of a Wheatstone bridge. The heat generated increases the electrical resistance of the filament that is measured and compared against calibrated standards.
- Ethane, hydrogen, and other combustible gases interfere in the test. H_2S interference can be reduced by adding solid NaOH to the container before sampling.

AIR ANALYSIS

Air collected in Tedlar bag; an aliquot of sample injected onto the GC column at ambient temperature; determined by TCD or FID.

- Use TCD if the methane concentration is expected to be more than 2000 ppm. In addition, the sample volume for packed column injection should be greater (~500 μL air). Detector response: 1–2 mg.
- A lower detection level may be obtained using an FID.
- GC column: molecular sieve 5A, 13X Chromosorb 102 (80/100 mesh), Carboxen 1004, Haye Sep Q, Carbosieve, Carbosphere, silica gel, activated alumina, or any other equivalent material. Fused silica nonpolar capillary column may be used for low sample volume.
- Alternatively, sample may be analyzed by GC/MS (using a capillary column) under cryogenic conditions.

  Characteristic mass: 15
  (1 ppm methane in air = 0.66 mg/m^3 at NTP)

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109 Methyl Bromide

Synonym: bromomethane; formula; CH_3Br; MW 94.95; CAS [74-83-9]; colorless gas with a chloroform-like smell at high concentrations; liquefies at 3.5°C; slightly soluble in water; miscible with organic solvents.

ANALYSIS OF AQUEOUS SAMPLES

Aqueous samples subjected to the purge and trap extraction method; volatile analyte adsorbed on the sorbent trap thermally desorbed and swept with helium onto a GC column for separation; detected by HECD, ECD, FID, or MSD; low retention time.

- Characteristic masses for GC/MS identification: 94 and 96.
- Limit of detection: in the range of 0.1 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
- Recommended surrogate/IS: bromochloromethane and 1,2-dichloroethane d_4.
- Samples collected in glass/plastic containers without headspace, refrigerated, and analyzed within 14 days.

See Chapter 32 for GC columns and conditions and for a detailed discussion.

AIR ANALYSIS

The following methods are recommended:

- Carbon molecular sieve adsorption; desorption at 350°C into a cryogenically cooled trap; flash evaporated onto a capillary column GC/MS system; recommended sample volume 10 L; flow rate 100 mL/min.
- Collected in SUMMA passivated canister; transferred into a cryogenically cooled trap attached to a GC column; determined by ECD or MSD.
- Precision and accuracy of the above methods not established.

(1 ppm methyl bromide in air = ~3.9 mg/m^3 at NTP)

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110 Methyl Chloride

Synonym: chloromethane; formula: CH_3Cl; MW 50.49; CAS [74-87-3]; colorless gas with a faint sweet odor; freezes at −32.7°C; slightly soluble in water; miscible with organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples subjected to the purge and trap extraction method; sample aliquot purged under helium flow; highly volatile methyl chloride transferred from the aqueous matrix to the vapor phase; absorbed on a sorbent trap; analyte thermally desorbed and swept onto a GC column for separation; detected by HECD, ECD, FID, or MSD; low retention time.
- Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water; subjected to purge and trap concentration and analyzed as above.
  - Alternatively, sample thermally desorbed under helium flow and analyzed as above.
  - Characteristic masses for GC/MS identification: 50 and 52.
  - Limit of detection: in the range 0.1 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: bromochloromethane and 1,2-dichloroethane-d_4.
  - Samples collected in glass/plastic containers without headspace, refrigerated, and analyzed within 14 days.

See Chapter 32 for GC columns and conditions and for a detailed discussion.

AIR ANALYSIS

- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into a cryogenically cooled trap attached to a GC column; the trap heated; the analyte separated on the column for detection by ECD, FID, or GC/MS (U.S. EPA Method TO-14).
- Adsorbed over a carbon molecular sieve (∼400 mg); heated to 350°C under helium purge; transferred into a cryogenic trap and flash evaporated onto a capillary column GC/MS; recommended sample volume 10 L; flow rate 100 mL/min; the precision and accuracy data for the compound is not established.

  (1 ppm methyl chloride in air = ∼2 mg/m^3 at NTP)

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111 Methylene Chloride

Synonyms: dichloromethane; formula: CH_2Cl_2; MW 84.94; CAS [75-09-2]; a volatile halogenated hydrocarbon; widely used as a solvent; boils at 40°C; vapor pressure 349 torr at 20°C; density 1.323 g/mL at 20°C; solubility in water, very low (1.3%) miscible in organic solvents; nonflammable.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted by the purge and trap method; sample purged under helium flow; volatile analyte thermally desorbed out from the sorbent trap and swept onto a GC column for separation; detected by HECD, ECD, FID, or MSD.
- Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water; subjected to purge and trap concentration and analyzed as above.
  - Alternatively, analyte thermally desorbed under helium flow and analyzed as above.
  - Characteristic masses for GC/MS identification: 84, 49, 51, and 86.
  - Limit of detection: in the range 0.3 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: bromochloromethane and 1,2-dichloroethane-d_4.
  - Samples collected in glass/plastic containers without headspace, refrigerated, and analyzed within 14 days.

See Chapter 32 for GC columns and conditions and a detailed discussion.

AIR ANALYSIS

Air analysis may be performed by NIOSH, OSHA, or EPA methods. The latter gives a lower range of detection.

- Adsorbed over coconut charcoal (100 mg/50 mg); desorbed with CS_2 and analyzed by GC-FID; flow rate 10–200 mL/min; sample volume 0.5–2.5 L (NIOSH 1987); sample volume 10 L for 350 mg sorbent (OSHA Method 59).
- Adsorbed over a carbon molecular sieve (~400 mg) in a cartridge; heated at 350°C under helium purge; transferred into a cryogenic trap and flash evaporated onto a capillary column GC/MS; recommended flow rate 1 L/min; sample volume 60 L (U.S. EPA Method TO-2).
- Collected in a trap in liquid argon; the trap removed and heated; sample transferred to a precooled GC column for ECD or HD detection (U.S. EPA Method TO-3).
- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into a cryogenically cooled trap attached to a GC column; the trap heated; the analyte separated on the column for detection by ECD, FID, or GC/MS (U.S. EPA Method TO-14).

(1 ppm methylene chloride in air = 3.47 mg/m^3 at NTP)

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112 Methyl Iodide

Synonym: iodomethane; formula CH_3I; MW 142.94; CAS [74-88-4]; used as a methylating agent and in microscopy; colorless liquid, turns yellow or brown on exposure to light or moisture; boils at 42.5°C; vapor pressure 375 torr at 20°C; freezes at −66.5°C; decomposes at 270°C; density 2.28 g/mL; low solubility in water (2%); soluble in alcohol and ether; toxic and carcinogenic.

ANALYSIS OF AQUEOUS SAMPLES

- A measured volume of sample purged by an inert gas; analyte trapped on a sorbent trap; transferred onto a GC column by heating the trap and backflushing with He; determined by GC/MS.
  - The characteristic masses for GC/MS identification: 142 and 127.
  - GC column: a fused silica capillary column such as DB-624, VOCOL, DB-5, or equivalent.
  - A halogen specific detector such as HECD may be used in the GC system.
  - Detection limit: in the range 0.02 mg/L for 25 mL sample volume.

AIR ANALYSIS

- Air drawn through a solid sorbent tube containing coconut shell charcoal (100 mg/50 mg); the analyte desorbed with 1 mL toluene (more than 8 h standing); toluene extract analyzed by GC-FID (NIOSH Method 1014, 1985); recommended air flow rate 0.5 L/min; sample volume 30 L.
  - GC column: Chromosorb 101 or equivalent.
  - For a 50 L air sample, the working range of this method is 10–100 mg/m^3.
- Suggested method: Alternatively, air sample collected in a SUMMA passivated stainless steel canister pressurized using a pump; canister attached to the analytical system; analyte concentrated by collection in a cryogenically cooled trap; cryogen removed; temperature of trap raised; analyte revolatilized and separated on a GC column; determined by a mass spectrometer.
  - No precision or accuracy data are available.
  - A fused silica capillary column such as VOCOL, DB-5, or equivalent should give satisfactory performance.
  - Methyl iodide may be identified from its retention time and the characteristic masses 142 and 127.

    (1 ppm methyl iodide in air = 5.80 mg/m^3 at NTP)

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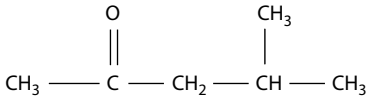
113 Methyl Isobutyl Ketone

Synonyms: MIBK, hexone, isopropyl acetone, 4-methyl-2-pentanone; formula $C_6H_{12}O$; structure:



MW 100.16; CAS [108-10-1]; used as a solvent for gums, resins, oils, and waxes; colorless liquid; faint camphor-like odor; boils at 117°C; vapor pressure 7.5 torr at 25°C; freezes at −87.4°C; density 0.80 g/mL; solubility in water 19.1 g/L, soluble in most organic solvents; flammable.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Purge and trap extraction method; MIBK purged out from the aqueous matrix under the He flow; thermally desorbed out from the sorbent trap and backflushed with He onto a GC column for separation from other volatile compounds; detected by a FID or a mass spectrometer.
  - Characteristic masses for GC/MS identification: 43 (primary ion), 58, and 85.
  - GC column: a 75 m × 0.53 mm ID × 3 mm film thickness fused silica capillary column such as DB-624 or equivalent.
  - Detection limit: in the range 0.25 mg/L for a 25 mL sample volume, detected by GC/MS.
  - Samples collected in a glass container without headspace, refrigerated, and analyzed in 14 days.
- Alternatively, a 100 mL aliquot of aqueous sample is pH adjusted to 3; treated with 2,4-dinitrophenylhydrazine (DNPH); heated at 40°C for an hour under gentle swirling; DNPH derivative extracted with methylene chloride by liquid–liquid extraction; extract solvent exchanged to acetonitrile; determined by HPLC-UV at 360 nm.
  - HPLC column: C-18 reverse phase column, such as Zorbax ODS or equivalent; mobile phase acetonitrile/water (70:30); flow rate 1 mL/min.
  - The DNPH derivative may alternatively be extracted by solid-phase extraction on a sorbent cartridge, conditioned with 10 mL dilute 1 M citrate buffer (1:25 dilution) and 10 mL saturated NaCl solution. The extract loaded on the cartridge, and the derivative eluted with acetonitrile for HPLC analysis.
  - The DNPH derivative of MIBK may be determined by GC instead of HPLC.
- A measured amount of the solid sample that is extracted with methanol is taken; an aliquot of methanol extract spiked into a measured volume of reagent water (25 mL) and subjected to purge and trap extraction and GC/MS determination as above.
- Alternatively, MIBK thermally desorbed out from the solid matrix under the He purge (without any solvent treatment) and analyzed by GC or GC/MS.

AIR ANALYSIS

- Air drawn through a solid sorbent tube packed with coconut shell charcoal (100 mg/50 mg); MIBK desorbed with 1 mL CS_2 (more than 30 min standing); analyzed by GC-HD (NIOSH Method 1300, 1989); recommended flow rate 0.1 L/min; sample volume 5 L.
  - GC column: 10% SP-2100 and 0.1% Carbowax 1500 on Chromosorb WHP or a fused silica capillary such as DB-I, DB-5, or equivalent.

- Alternatively, air drawn through an impinger solution containing 2 N HCl solution of 0.05% DNPH reagent and isooctane; the DNPH derivative of MIBK partitions into isooctane; aqueous layer extracted with hexane/methylene chloride mixture (70:30); extract combined with isooctane; the three solvent mixture evaporated to dryness under N_2 stream; residue dissolved in methanol; analyzed by HPLC-UV as above (U.S. EPA, 1999. Method TO-5).
  - Recommended airflow rate 200 mL/min; sample volume 20 L.
  - Isooctane volume: 10–20 mL.
- Alternatively, DNPH coated silica gel or Florisil adsorbent may be used instead of impinger solution; derivative eluted with acetonitrile for HPLC determination.

(1 ppm MIBK in air = 4.10 mg/m^3 at NTP)

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114 Methyl Isocyanate

Synonyms: isocyanic acid methyl ester, isocyanatomethane, MIC; formula: $CH_3N{=}C{=}O$; MW 57.05; CAS [624-83-9]; used in the manufacture of carbamate pesticides; colorless liquid with an unpleasant odor; boils at 39°C; freezes at −80°C; vapor pressure 400 torr at 20°C; density 0.96 g/mL at 20°C; vapor density 1.97 (air = 1); decomposes in water; soluble in most organic solvents; highly toxic and flammable.

AIR ANALYSIS

- Air drawn through a glass tube containing ion exchange resin XAD-2; MIC desorbed from the resin into a solution of fluorescamine (Fluram) in tetrahydrofuran; an intense fluorescent derivative formed; derivative analyzed by HPLC using a multiwavelength fluorescent detector (Vincent and Ketcham, 1980); recommended air flow rate 200 mL/min; sample volume 15 L.
  - The detection limit is 0.02 ppm.
  - Chemical name for fluorescamine is 4-phenylspiro[furan-2(3 H),l-phthalan]3,3′-dione.
  - Silica gel may be alternatively used as an adsorbent; the method sensitivity, however, is greater with Amberlite XAD-2.
  - Monomethylamine interferes in the test; interference is removed by passing air through an impinger containing 0.5% $CuCl_2$ solution before drawing the air through the solid adsorbent.
  - A reverse phase column, such as Varían CH-10 or equivalent, is suitable for separation.

  (1 ppm MIC in air = 2.33 mg/m^3 at NTP)

REFERENCE

Vincent, W.J. and N.H. Ketcham. 1980. *Analytical Techniques in Occupational Health Chemistry.* ACS Symposium Series, vol. 120, pp. 121–147.

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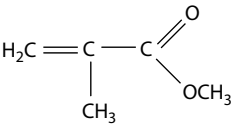
115 Methyl Methacrylate

Synonym: methacrylic acid, methyl ester; formula: $C_5H_8O_2$; structure:



MW 100.12; CAS [80-62-6]; used in the manufacture of plastics and resins; colorless liquid; polymerizes; boils at 100°C; vapor pressure 35 torr at 20°C; density 0.944 g/mL; soluble in benzene, chloroform, tetrahydrofuran, and methyl ethyl ketone.

ANALYSIS OF AQUEOUS SAMPLES

- A measured volume of sample purged with an inert gas; analyte adsorbed on a sorbent trap; trap heated and backflushed with He to desorb the analyte into a capillary GC column interfaced to a mass spectrometer (MS); determined on the MS.
  - Characteristic masses for GC/MS identification: 69 (primary ion) and 99.
  - GC column: a fused silica capillary column, such as VOCOL, DB-624, or equivalent.
  - Detection limit: in the range 0.5 mg/L when the sample volume is 25 mL.
  - Methylmethacrylate polymerizes quickly. The sample must be collected without headspace, refrigerated, and analyzed immediately.

AIR ANALYSIS

- Air drawn through a solid sorbent tube packed with XAD-2 (400 mg/200 mg); analyte desorbed with 2 mL CS_2; extract analyzed by GC-FID (NIOSH Method 2537, 1989); recommended air flow rate 0.05 L/min; sample volume 5 L.
  - GC column: a fused silica capillary column; DB-1, 30 m × 0.25 mm × 1 mm or equivalent; packed column: 10% FFAP on Supelcoport (120/100 mesh) or equivalent.
  - Analyte adsorbed on the trap is stable for 30 days, if refrigerated; stable for 7 days at 25°C.
  - The working range is 10–1000 mg/m^3 for a 3 L air sample.

    (1 ppm methylmethacrylate in air = 4.10 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Safety and Health. 1989. *NIOSH Manual of Analytical Methods*, 3rd edition and update. Cincinnati, OH: National Institute for Occupational Safety and Health.

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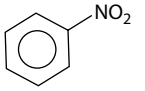
116 Nitrobenzene

Synonyms: nitrobenzol, mirbane oil; formula: $C_6H_5NO_2$; structure:



MW 123.12; CAS [98-95-3]; a pale yellow oily liquid; boils at 210°C; solidifies at −6°C; density 1.205 g/mL at 15°C; miscible in most organic solvents; slightly soluble in water (0.2%); toxic.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted with methylene chloride; extract concentrated and solvent exchanged to hexane; Florisil cleanup (for dirty samples); extract analyzed on GC using FID or NPD in N-mode or by GC/MS.
- Soil, sediment, or solid waste samples extracted with methylene chloride by sonication or Soxhlet extraction; extract concentrated, exchanged to hexane (for Florisil cleanup), and determined as above.
  - Column-packed: 1.95% QF-1/1.5% OV-17 on Gas-Chrom Q (80/100 mesh), 3% OV-101 on Gas-Chrom Q (80/100 mesh), or 3% SP-2250 on Supelcoport; capillary: PTE-5, SPB-5, DB-5, Rtx-5 or equivalent.
  - FID response: ∼10 ng.
  - Characteristic masses for GC/MS identification: 77, 123, and 65.
  - Suggested surrogate/IS: aniline d_5, 4-fluoroaniline, and 1-fluoronaphthalene.
  - Samples collected in glass containers, refrigerated, extracted within 7 days of collection, and analyzed within 40 days of extraction.

AIR ANALYSIS

- Analyte adsorbed over silica gel in a solid sorbent tube; desorbed with methanol in an ultrasonic bath for 1 h; analyzed by GC-FID using a suitable column (i.e., 10% FFAP on Chromosorb W-HP) (NIOSH Method 2005, 1984); recommended flow rate 0.05–1 L/min; sample volume 50–150 L.
- Adsorbed over Tenax (2 g) in a cartridge; cartridge heated under the He purge; analyte transferred successively onto a cold trap and then to a precooled GC column; column heated; analyte eluted and determined by GC-FID or GC/MS; recommended flow rate 0.5 L/min; sample volume 100 L.
- Collected in a trap in liquid argon; the trap removed and heated; sample transferred onto a precooled GC column for FID detection.

(1 ppm nitrobenzene in air = 5 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Safety and Health 1984. *NIOSH Manual of Analytical Methods*, 3rd edn. Cincinnati, OH: National Institute for Occupational Safety and Health.

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117 Nitrogen Dioxide

Synonyms: nitrogen peroxide; formula: NO_2; MW 46.01; CAS [10102-44-0]; occurs in automobile exhaust and cigarette smoke; produced by the reaction of nitric acid with metals, decomposition of nitrates, or during fire; reddish-brown fuming liquid or gas; sharp pungent odor; liquefies at 21°C; solidifies at −9.3°C; density of liquid 1.45 at 20°C; vapor 1.58 (air = 1); reacts with water to form nitric acid and nitrogen oxide; reacts with alkalies to form nitrates and nitrites; highly toxic.

AIR ANALYSIS

Analysis may be performed by using passive indicator tubes, various passive samplers, and electrochemical instruments.

- Air drawn through Palmes tube with three triethanolamine (TEA)-treated screens; analyte converted into nitrite ion (NO_2^-;NO_2^-) treated with an aqueous solution of a reagent mixture containing sulfanilamide, H_3PO_4, and *N*-1-naphthyl-ethylenediamine dihydrochloride; color develops; absorbance measured at 540 nm by a spectrophotometer; concentration determined from a standard calibration curve made from $NaNO_2$ (NIOSH Method 6700, 1984).
  - Alternatively, a bubbler may be used instead of Palmes tube; NO_2^- measured by colorimetry as above.
- Concentration of NO_2 may be measured directly by passive colorimetric dosimeter tubes (i.e., Vapor Guard); NO_2 in air diffuses into the tube; color changes (white to brown in Vapor Guard); concentration determined from the length of stain.
  - Temperature and relative humidity may affect measurement; tubes should be used between 15°C and 40°C.

  (1 ppm NO_2 = 1.88 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Safety and Health. 1984. *NIOSH Manual of Analytical Methods*, 3rd edn. Cincinnati, OH: National Institute for Occupational Safety and Health.

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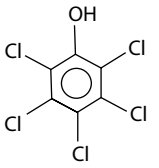
118 Pentachlorophenol

Synonym: pentachlorophenate; formula: C_6Cl_5OH; structure:



MW 166.32; CAS [87-86-5]; crystalline solid melts at 190°C; insoluble in water (14 ppm at 20°C), soluble in organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples pH adjusted to below 2; extracted with methylene chloride; extract concentrated and analyzed by GC-FID or GC/MS.
- Alternatively, extract exchanged into 2-propanol; derivatized with pentafluorobenzyl bromide; derivative dissolved in hexane; fractionated over silica gel; eluted with 15% toluene in hexane and determined by GC-ECD.
- Aqueous samples may be analyzed by HPLC using a C-18 derivatized reverse phase column or on an underivatized polystyrene-divinylbenzene column such as Poly-RP CO (Alltech, 1995); gradient: acetonitrile and 0.01 M K_3PO_4 at pH 7 (55:45) and the analyte detected by UV at 254 nm.
- Soil, solid waste, and sludge extracted with methylene chloride by sonication, Soxhlet or supercritical fluid extraction; extract may be acid washed, concentrated, and analyzed by GC-FID, GC-ECD, or GC/MS as above.
- Characteristic masses for GC/MS determination: 266, 264, and 268 (electron impact ionization); 267, 265, and 269 (chemical ionization).
- Limit of detection: in the range 5–10 μg/L on FID or GC/MS and below 1 μg/L on ECD (for aqueous samples concentrated by 1000 times).
- Recommended surrogate/IS: pentafluorophenol and 2-perfluoromethyl phenol.
- Samples collected in glass containers, refrigerated, and extracted within 7 days of collection and analyzed within 40 days of extraction.

See Chapter 49 for GC columns and conditions.

AIR ANALYSIS

- Not likely to occur in ambient air in vapor state; the vapor pressure too low (0.00017 torr at 20°C).
- Airborne particles collected on a sorbent cartridge containing polyurethane foam; extracted with 5% diethyl ether in hexane; extract analyzed by GC-ECD; recommended air flow 5 L/min; sample volume 1000 L (U.S. EPA Method TO-10).

REFERENCES

Alltech Corporation, 1995. *Product Catalog and Literature*, Deerfield, IL.

US EPA. 1999. *Method TO 10A: Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatography Multi-Detector (GC/MD) Detection, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd edn. Cincinnati, OH: Center for Environmental Research Information, Office of Research and Development.

119 Phosgene

Synonyms: carbonyl chloride, carbon oxychloride, chloroformyl chloride; formula: $COCl_2$; structure: $O{=}CCl_2$; MW 98.91; CAS [75-44-5]; formed in air in trace amounts by photodecomposition of chlorinated solvent vapors; used in the synthesis of dyes and pesticides, and as a war gas; colorless; suffocating odor at low ppm concentration; sweet hay-like odor at low ppb concentration; liquefies at 8°C; solidifies at −118°C; density 1.43 g/mL at 0°C; slightly soluble in water (reacting slowly), soluble in hexane, benzene, and glacial acetic acid; highly poisonous.

AIR ANALYSIS

- Air drawn through a midget impinger containing 10 mL of 2% aniline in toluene (by volume); phosgene reacts with aniline forming carbanilide (1,3-diphenylurea); solvent evaporated at 60°C under N_2 flow; residue dissolved in 1 mL acetonitrile; carbanilide analyzed by reverse-phase HPLC with an UV detector set at 254 nm (EPA, 1999. Method T06); recommended flow rate 200 mL/min; sample volume 20 L.
- A C-18 reverse-phase column such as Zorbax ODS or equivalent may be used.
- Chloroformates and acidic substances (at high concentrations) may interfere in the test.
- Detection limit: in the range of 0.1 ppb.
- Air drawn through an impinger containing 4,4′-nitrobenzyl pyridine in diethyl phthalate; phosgene forms a colored derivative; absorbance measured by a spectrophotometer.
- Detection limit: in the range of 10 ppb.
- Air drawn through a midget impinger containing a 10% solution of equal parts of ρ-dimethylaminobenzaldehyde and diphenylamine in carbon tetrachloride; phosgene reacts forming a deep orange derivative; absorbance measured by a spectrophotometer and compared against a standard calibration curve.
- The method applicable to measure low ppm concentration.
  (1 ppm phosgene in air = 4 mg/m^3 at NTP)

REFERENCE

US EPA. 1999. *Method TO 6: Method for the Determination of Phosgene in Ambient Air Using High Performance Liquid Chromatography, Compendium Methods for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd edn. Cincinnati, OH: Center for Environmental Research Information, Office of Research and Development.

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120 Pyridine

Synonyms: azabenzene, azine; formula: C_5H_5N; structure:

CAS [110-86-1]; used as a solvent and an intermediate in organic synthesis; colorless liquid; characteristic disagreeable odor; boils at 115°C; freezes at −41.5°C; density 0.98 g/mL; miscible with water and most organic solvents; weak base; toxic and flammable.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- A measured volume of aqueous sample is pH adjusted to >11 and then mixed and shaken repeatedly with methylene chloride; pyridine being basic, partitions into the organic layer while acidic compounds partition into the basic aqueous phase; aqueous layer discarded; organic solvent extract concentrated and separated on a GC column; determined by a mass spectrometer, a NPD or a FID.
- A measured quantity of soil, sediment, or solid waste sample is extracted with a measured volume of water; aqueous solution is pH adjusted to >11 and serially extracted with methylene chloride; pyridine partitions into the organic phase that is then concentrated and analyzed as above.
- Characteristic mass for GC/MS identification: 79.
- GC column: silicone-coated fused silica capillary column, such as DB-5 or equivalent.
- Precision, accuracy, and the detection limit for pyridine have not been determined.

AIR ANALYSIS

- Air drawn through a solid sorbent tube packed with coconut shell charcoal (100 mg/50 mg); pyridine desorbed with 1 mL methylene chloride (more than 30 min standing); eluant analyzed by GC-HD (NIOSH method 1613, 1987); recommended air flow rate 0.5 L/min; sample volume 100 L.
- GC column: 3 m × 3 mm stainless steel packed with 5% Carbowax 20 M on 80/100 mesh acid-washed DMCS Chromosorb W or a silicon-coated fused silica.
- Capillary column (e.g., DB 1) may be used. The working range for this method was determined to be 1–14 ppm for a 100 L air sample.
  (1 ppm pyridine in air = 3.23 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Safety and Health. 1987. *NIOSH Manual of Analytical Methods*, 3rd edition and updates. Cincinnati, OH: National Institute for Occupational Safety and Health.

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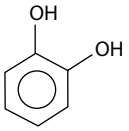
121 Pyrocatechol

Synonyms: 2-hydroxyphenol, *o*-diphenol, 1,2-benzenediol, *o*-dihydroxybenzene; formula: $C_6H_5O_2$; structure:



An isomer of resorcinol; MW 110.12; CAS [120-80-9]; used in photography and dyeing fur; crystalline solid; melts at 105°C; soluble in water and most organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

Recommended method:

- Aqueous samples pH adjusted to below 2; extracted with methylene chloride; extract concentrated and analyzed by GC-FID or GC/MS.
- Alternatively, extract exchanged into 2-propanol; derivatized with pentafluorobenzyl bromide, and determined by GC-ECD.
- Soil, solid waste, and sludge mixed with anhydrous Na_2SO_4 and extracted with methylene chloride by sonication or Soxhlet extraction; extract may be acid washed, concentrated, and analyzed by GC-FID, GC-ECD, or GC/MS as above.
- Characteristic masses for GC/MS determination: 110, 81, and 82.
- Limit of detection: in the range 100 μg/L for aqueous samples concentrated by 1000 times; GPC cleaned and determined by GC/MS.
- Recommended surrogate/IS: 2-fluorophenol and pentafluorophenol.
- Samples collected in glass containers, refrigerated, extracted within 7 days of collection, and analyzed within 40 days of extraction.

See Chapter 44 for GC columns and conditions.

AIR ANALYSIS

- Recommended method: airborne particles collected on a sorbent cartridge containing polyurethane foam; particulates deposited on the filter extracted with methylene chloride; extract analyzed by GC-FID or GC/MS; recommended air flow 5 L/min; sample volume 1000 L.

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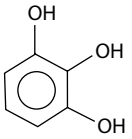
122 Pyrogallol

Synonyms: 1,2,3-trihydroxybenzene; pyrogallic acid; 1,2,3-benzenetriol; formula: $C_6H_5O_3$; structure:



MW 126.12; CAS [87-66-1]; white crystalline solid; melts at 132°C; soluble in water and most organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples pH adjusted to below 2; extracted with methylene chloride; extract concentrated and analyzed by GC-FID or GC/MS.
- Alternatively, extract exchanged into 2-propanol; derivatized with pentafluorobenzyl bromide and determined by GC-ECD.
- Aqueous samples directly injected onto the GC column for FID determination.
- Soil, solid waste, and sludge extracted with methylene chloride by sonication, Soxhlet, or supercritical fluid extraction; extract may be acid washed, concentrated, and analyzed by GC-FID, GC-ECD, or GC/MS as above.
- Recommended surrogate/IS: 2-fluorophenol and pentafluorophenol.
- Samples collected in glass containers, refrigerated, extracted within 7 days of collection, and analyzed within 40 days of extraction.

See, Chapter 44 for GC columns and conditions.

AIR ANALYSIS

- Not likely to occur in ambient air in vapor state; vapor pressure too low.
- Recommended method to analyze airborne particles: air drawn through a sorbent cartridge containing polyurethane foam; deposited particles extracted with methylene chloride; extract analyzed by GC-FID or GC/MS; recommended airflow 5 L/min; sample volume 1000 L.

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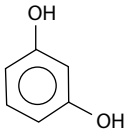
123 Resorcinol

Synonyms: *m*-hydroxyphenol; 3-hydroxyphenol; 1,3-benzenediol; 1,3-dihydroxybenzene, formula: $C_6H_6O_2$; structure:



An isomer of pyrocatechol; MW 110.12; CAS [108-46-3]; used in the manufacture of resins, dyes, and explosives; white crystalline solid; melts at 110°C; boils at 214°C; soluble in water, alcohol, and ether; slightly soluble in chloroform.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples are pH adjusted to below 2; extracted with methylene chloride; extract concentrated and analyzed by GC-FID or GC/MS.
- Alternatively, extract exchanged into 2-propanol; derivatized with pentafluorobenzyl bromide and determined by GC-ECD.
- Soil, solid waste, and sludge mixed with anhydrous Na_2SO_4, extracted with methylene chloride by sonication or Soxhlet extraction; extract may be acid washed, concentrated, and analyzed by GC-FID, GC-ECD, or GC/MS as above.
- Characteristic masses for GC/MS determination: 110, 81, 82, 53, and 69.
- Limit of detection: in the range of 100 μg/L for aqueous samples, concentrated by 1000 times, extract GPC cleaned and determined by GC/MS.
- Recommended surrogate/IS: 2-fluorophenol and pentafluorophenol.
- Samples collected in glass containers, refrigerated, extracted within 7 days of collection, and analyzed within 40 days of extraction.

See Chapter 44 for GC columns and conditions.

AIR ANALYSIS

- Recommended method: airborne particles collected on a sorbent cartridge containing polyurethane foam; deposited particles extracted with methylene chloride; extract analyzed by GC-FID or GC/MS; recommended airflow 5 L/min; sample volume 1000 L.

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124 Stibine

Synonyms: antimony hydride, hydrogen antimonide; formula SbH_3; MW 124.78; CAS [7803-52-3]; used as a fumigating agent; colorless gas with a disagreeable odor; decomposes slowly at ambient temperature; liquefies at −18°C; gas density 5.515 g/L; slightly soluble in water, dissolves in organic solvents; highly toxic; flammable gas.

AIR ANALYSIS

- Air drawn through a solid sorbent tube containing $HgCl_2$-coated silica gel (1000 mg/500 mg); stibine extracted out from the sorbent trap with 15 mL conc. HCl (over 30 min swirling); acid extract diluted to a measured volume; an aliquot of the sample extract treated with ceric sulfate, followed by isopropyl ether and water; mixture transferred into a separatory funnel and shaken; aqueous layer discarded; ether extract treated with Rhodamine B solution and shaken; phases allowed to separate; an aliquot of organic phase centrifuged; color developed due to antimony measured by a spectrophotometer at 552 nm (NIOSH method 6008, 1987); recommended air flow rate 0.1 L/min; sample volume 20 L.
- Concentration of antimony is read from a standard calibration curve.
- Antimony in HCl extract may also be measured by atomic absorption or ICP emission spectrometry.
- Certain metals such as gold, iron(III), thallium (I), and tin(II) at high concentrations interfere in the above colorimetric analysis (iron (III) interferes at >30,000 mg, while the other metals interfere at >1000 mg).
- Color forming reagent, Rhodamine B solution should have a strength of 0.01% in 0.5 M HCl.
- The working range is 0.02–0.7 ppm for a 20 L air sample.
- Sample is stable at least for 7 days at 25°C.
- Use a cellulose ester membrane if paniculate antimony compounds are suspected to be present in the air.
- Activated charcoal absorbent showed poor collection efficiency.
  (1 ppm stibine in air = 5.10 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Safety and Health. 1987. *NIOSH Manual of Analytical Methods*, 3rd edition and updates. Cincinnati, OH: National Institute for Occupational Safety and Health.

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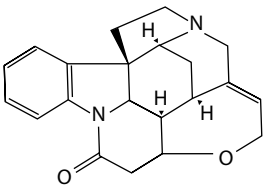
125 Strychnine

Synonym: strychnidin-10-one; formula: $C_{21}H_{22}N_2O_2$; structure:



MW 334.40; CAS [57-24-9]; used as a rodent poison; white crystalline powder; highly bitter, melts at 268°C; solubility in water (0.16 g/L); moderately soluble in hot alcohol; dissolves readily in chloroform; highly toxic.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

A measured volume of aqueous sample acidified to pH <2 and serially extracted with methylene chloride; strychnine being basic, partitions into the aqueous phase; organic layer discarded; aqueous phase is pH adjusted to >10 and serially extracted with methylene chloride; solvent extract concentrated; analyzed by GC/MS.

- Characteristic masses for GC/MS identification: 334, 335, and 333.
- GC column: a fused silica capillary column, such as DB-5, SPB-5, or equivalent; the compound is eluted relatively at a long retention time.

A measured quantity of solid sample mixed with anhydrous Na_2SO_4; the mixture sonicated or Soxhlet extracted with methylene chloride or chloroform; solvent extract concentrated; cleanup (if required) by acid–base partitioning; analyzed as above by GC/MS using an appropriate column.

Alternatively, a measured quantity of solid sample extracted with aqueous 1-heptane sulfonic acid and acetonitrile; the solution analyzed by HPLC using an UV detector at 254 mm (HPLC column and conditions given in Chapter 10.

- No precision and accuracy study data are available for the above method.

AIR ANALYSIS

Air drawn through a 37-mm glass fiber filter; strychnine deposited on the filter, desorbed with 5 mL mobile phase for HPLC-UV detection at 254 mm (NIOSH method 5016, 1985); recommended air flow rate 2 L/min; sample volume 500 L.

- The mobile phase for HPLC analysis, as well as the solvent media for desorption-aqueous 1-heptane sulfonic acid and acetonitrite mixture; pH 3.5; flow rate 1 mL/min at ambient temperature.
- HPLC column: packed with M-Bondapak C-18, 10 mm particle size.
- The working range for the above method is 0.05–10 mg/m^3 for a 200 L of air sample.

REFERENCE

National Institute for Occupational Safety and Health. 1985. *NIOSH Manual of Analytical Methods*, 3rd edition and updates. Cincinnati, OH: National Institute for Occupational Safety and Health.

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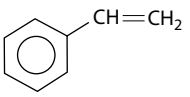
126 Styrene

Synonyms: vinylbenzene, phenylethylene, ethenylbenzene; formula: C_8H_8; structure:



MW 104.14; CAS [100-42-5]; used for manufacturing plastics, resins, and synthetic rubber; colorless to yellowish oily liquid; penetrating odor; slowly polymerizes on exposure to light and air; boils at 145°C; vapor pressure 6.1 Torr at 25°C; freezes at −31°C; density 0.906 g/mL at 20°C; sparingly soluble in water, miscible with most organic solvents; forms peroxide.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- A measured volume of the sample is purged with an inert gas; styrene purged out from water; absorbed on a sorbent trap; trap heated and back flushed with He; analyte transported into the GC column; separated from other volatiles; determined on a PID, FID or a mass spectrometer.
- Solid samples mixed with methanol; an aliquot of methanol extract spiked into a measured volume of water (25 mL) in the purging vessel; subjected to purge and trap concentration and analyzed as above.
- GC column: a fused silica capillary column, such as VOCOL, DB-624, or equivalent; packed column: 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent.
- Characteristic masses for GC/MS identification: 104, 103, 78, and 51.
- Recommended surrogate/IS: ethyl benzene-d_5 (*m/z* 114, 63, 88).
- Limit of detection: in the range 0.5 mg/L for a 5 mL sample volume, when detected by PID.
- Samples collected in glass containers without headspace, refrigerated, and analyzed immediately. Because styrene undergoes polymerization, oxidation, and addition reactions, exposure to sunlight or air should be avoided, and analysis should be done immediately. Preservation of sample with HCl is not recommended due to its formation of an additional product.

AIR ANALYSIS

- Air drawn through a sorbent tube packed with coconut shell charcoal (100 mg/50 mg); analyte desorbed into CS_2 (more than 30 min standing); the eluant analyzed by GC-FID (NIOSH method 1501, 1984); recommended airflow rate 100 mL/min; sample volume 20 L.
- GC column: packed with 10% OV-275 on 100/120 mesh Chromosorb W-AW, Porapak P (50/80 mesh), or equivalent.
- Alternatively, air drawn through a cartridge packed with carbon molecular sieve (0.5 g); cartridge heated at 350°C under He purge; analyte transferred to the front of a precooled

GC column; temperature programmed; styrene determined on a PID, FID, or a mass spectrometer; recommended airflow rate 0.5 L/min; sample volume 50 L.

- No precision and accuracy data available for this method.

(1 ppm styrene in air = 4.26 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Safety and Health. 1984. *NIOSH Manual of Analytical Methods*, 3rd edn. Cincinnati, OH: National Institute for Occupational Safety and Health.

127 Sulfur Dioxide

Formula: SO_2; MW 64.06; CAS [7446-09-5]; a major air pollutant; produced when soft coals, oils, and automobile fuels burn; used as a fumigating and bleaching agent; colorless gas with a strong suffocating odor; liquefies at −10°C; solidifies at −72°C; soluble in water (8.5% at 25°C), alcohol, ether, and chloroform; highly toxic and a strong irritant.

AIR ANALYSIS

- Air drawn through two 0.8 μm cellulose ester membranes: (1) the front filter to collect any interfering particulate sulfate and sulfite in the air and (2) the back filter, treated with KOH to trap SO_2; SO_2 converted to K_2SO_3 on the back filter; this filter treated with a 10 mL mixture solution of 3 mmol $NaHCO_3$ and 2.4 mmol Na_2CO_3; K_2SO_3 dissociates into SO_3^{2-} anion, which is then determined by ion chromatography (NIOSH Method 6004, 1989); recommended flow rate 1 L/min; sample volume 100 L.
  - Use SO_3^{2-} calibration standard to determine the mass of SO_3^{2-}; a blank analysis performed on the media blanks for background correction.
  - Multiply SO_3^{2-} concentration by the stoichiometric factor 0.8 to calculate the concentration of SO_2.
  - Bicarbonate–carbonate eluant of the back filter may also be oxidized with a drop of 30% H_2O_2 to SO_4^{2-}; SO_4^{2-} formed measured by ion chromatography; to calculate the concentration of SO_2, multiply the mass of SO_4^{2-} found in the analysis, multiplied by the stoichiometric factor 0.667.
- Alternatively, air drawn through an impinger solution containing 0.3 N H_2O_2; SO_2 converted to SO_4^{2-} that is measured by titration with NaOH or barium perchlorate (NIOSH Method S308, 1978).
- Alternatively, air drawn through a solid sorbent tube containing molecular sieve 5A; SO_2 adsorbed on this trap desorbed on heating under He purge; transported onto GC column and determined by GC/MS.
  - Characteristic mass for SO_2 is 64.
- A passive colorimetric dosimeter tube may also be used for direct measurement; SO_2 diffuses into the tube; color changes (red-purple to yellow in Vapor Guard tube); concentration determined from the length of stain.
  - Temperature and relative humidity may affect measurement; tubes should be used between 15°C and 40°C.

(1 ppm $SO_2 = 2.62$ mg/m^3 at NTP)

REFERENCES

National Institute for Occupational Safety and Health. 1989. *NIOSH Manual of Analytical Methods*, 3rd edition and updates. Cincinnati, OH: National Institute for Occupational Safety and Health.

National Institute for Occupational Safety and Health. 1978. *NIOSH Manual of Analytical Methods*, 2nd edn. Cincinnati, OH: National Institute for Occupational Safety and Health.

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128 Tetrachloroethylene

Synonyms: perchloroethylene, tetrachloroethene, ethylene tetrachloride; formula: $Cl_2C{=}CCl_2$; MW 165.82; CAS [127-18-4]; used in dry cleaning and metal degreasing; colorless liquid with ether-like odor; boils at 121°C; freezes at −22°C; vapor pressure 19 Torr at 25°C; density 1.62 g/mL at 20°C; insoluble in water; miscible with organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted by the purge and trap method; analyte thermally desorbed out of the trap and swept onto a GC column for separation from other volatile compounds; detected by HECD, ECD, FID, or MSD.
- Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water; subjected to purge and trap concentration and analyzed as above.
- Methanol or hexane extract may be directly injected for GC (ECD or FID) or GC/MS determination.
  - Characteristic masses for GC/MS identification: 164, 129, 131, and 166.
  - Limit of detection: in the range 0.05 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: 2-bromo-1-chloropropane and 1,4-dichlorobutane.
  - Samples collected in glass/plastic containers without headspace, refrigerated, and analyzed within 14 days.

See Chapter 32 for chromatographic GC columns and conditions and a further discussion.

AIR ANALYSIS

- Adsorbed over coconut charcoal (100 mg/50 mg); desorbed with CS_2 and analyzed by GC-FID (NIOSH Method 1003, 1987); recommended flow rate 100 mL/min; sample volume 3 L.
- Adsorbed over Tenax (∼2 g) in a cartridge; desorbed by heating under the He purge; transferred into a cold trap and then to the front of a GC column at −70°C; column heated; analyte detected by ECD or MSD (U.S. EPA Method TO-1); recommended flow rate 100 mL/min; sample volume 10 L.
- Adsorbed over carbon molecular sieve (∼400 mg) in a cartridge; heated at 350°C under He purge; transferred into a cryogenic trap and flash evaporated onto a capillary column GC/MS (U.S. EPA Method TO-2); recommended flow rate 1 L/min; sample volume 100 L.
- Collected in a trap in liquid argon; the trap removed and heated; sample transferred to a precooled GC column for ECD or FID detection (U.S. EPA Method TO-3).
- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into cryogenically cooled trap attached to a GC column; the trap heated; the analyte separated on the column for detection by ECD or GC/MS (U.S. EPA Method TO-14).

(1 ppm tetrachloroethylene in air = ∼6.8 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Safety and Health. 1987. *NIOSH Manual of Analytical Methods*, 3rd edition and update. Cincinnati, OH: National Institute for Occupational Safety and Health.

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129 Tetraethyllead

Synonyms: tetraethylplumbane, lead tetraethyl; formula: $Pb(C_2H_5)_4$; MW 323.47; CAS [78-00-2]; used in motor gasoline as an additive to prevent "knocking"; such an application, however, is currently curtailed because of environmental pollution; boils at 200°C; vapor pressure 0.2 Torr at 20°C; density 1.653 g/mL at 20°C; insoluble in water; slightly soluble in alcohols; dissolves in benzene, toluene, hexane, petroleum ether, and gasoline; highly toxic (Patnaik, 2007).

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples may be microextracted with toluene, benzene, or hexane and the extract analyzed by GC/MS.
  - The *m/z* of primary characteristic ion 237; the secondary ions for compound identification 295, 208, 235, and 266 (electron impact ionization); peak intensity ratios for *m/z* 237:295:208 = 100:73:61 (Hites, 1992).
  - GC column: a fused silica capillary column such as DB-5, SPB-5, Rtx-5, or equivalent.
- Soil, sediments, or other nonaqueous matrices mixed with anhydrous Na_2SO_4 and extracted by sonication; the solvent extract analyzed as above by GC/MS.
  - If lead analysis is performed by AA spectrophotometry, following acid digestion of samples, then the stoichiometric calculation for tetraethyllead (TEL) may be done as follows:

$$\text{Concentration of TEL} = \text{conc. of Pb} \times 1.56$$

(Assuming that all Pb in the sample occurs as TEL; such an assumption, however, could be erroneous.)

REFERENCES

Hites, R.A. 1992. *Handbook of Mass Spectra of Environmental Contaminants*, 2nd edn. Boca Raton, FL: CRC Press.

Patnaik, P. 2007. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 3rd edn. New York: John Wiley and Sons.

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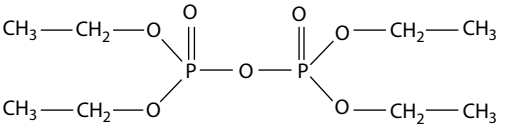
130 Tetraethyl Pyrophosphate

Synonyms: pyrophosphoric acid tetraethyl ester, TEPP; formula: $C_8H_{20}O_7P_2$; structure:



MW 290.19; CAS [107-49-3]; an organophosphorus pesticide; colorless liquid; hygroscopic; boiling point 124°C at 1 mm Hg; vapor pressure 0.00047 Torr at 20°C; decomposes at 170°C–213°C; density 1.185 g/mL at 20°C; miscible with most organic solvents; miscible with water but rapidly hydrolyzed; highly toxic.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples (TEPP unstable) extracted serially with methylene chloride; the extract concentrated and analyzed by GC/MS.
  - Characteristic masses for GC/MS identifications: 99, 155, 127, 81, and 109.
  - GC column: a fused silica capillary column, such as DB-5 or equivalent.
- Soil, sediment, or solid waste sample mixed with anhydrous Na_2SO_4; sonicated or Soxhlet extracted with methylene chloride; extract concentrated and analyzed by GC/MS as above.

AIR ANALYSIS

- Air drawn through a solid sorbent tube containing Chromosorb 102 (100 mg/50 mg); analyte desorbed with 1 mL toluene (on 60 min standing); toluene extract analyzed by GC-FPD (NIOSH method 2504, 1984); recommended flow rate 0.1 L/min; sample volume 20 L.
  - GC column: Super-Pak 20 M or equivalent.
  - Calibration standards are made from TEPP in toluene.
  - The working range of the method was determined to be 0.025–0.15 mg/m^3 for a 40 L sample.

    (1 ppm TEPP in air = 11.86 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Safety and Health. 1984. *NIOSH Manual for Analytical Methods*, 3rd edn. Cincinnati, OH: National Institute for Occupational Safety and Health.

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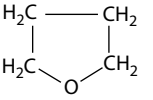
131 Tetrahydrofuran

Synonyms: oxolane, 1,4-epoxybutane, oxacyclopentane; formula: C_4H_8O; structure:



MW 72.12; CAS [109-99-9]; used as a solvent; colorless liquid; ether-like odor; boils at 66°C; vapor pressure 145 Torr at 20°C; freezes at −188.5°C; density 0.89 g/mL at 20°C; miscible with water and most organic solvents; highly flammable.

ANALYSIS OF AQUEOUS SAMPLES

- Aqueous samples extracted by the purge and trap method; the sorbent trap heated and backflushed with He to transfer the analyte onto a capillary GC column interfaced to a mass spectrometer; determined by GC/MS.
  - Because of high solubility of tetrahydrofuran in water, its purging efficiency is low. The purging vessel should be heated.
  - The characteristic masses for GC/MS identification: 71 (primary), 72, and 42.
  - GC column: a fused silica capillary column such as DB-624, 75 m × 0.53 mm × 3 mm, or equivalent.
- Alternatively, aqueous samples directly injected onto the GC column for FID determination.
  - The detection range on FID without sample concentration is several orders higher than the purge and trap method (under heating or purging vessel).
  - No precision and accuracy data are available for either of the above methods.

AIR ANALYSIS

- Air drawn through a solid sorbent tube containing coconut shell charcoal (100 mg/50 mg); analyte desorbed into 0.5 mL CS_2 (on 30 min contact time); the CS_2 extract analyzed by GC-FID (NIOSH method 1609, 1985); recommended airflow rate 0.1 L/min; sample volume 5 L.
  - GC column: stainless steel column packed with Porapak Q (50/80 mesh). A fused silica capillary column such as DBWAX or DB-624 may also be used.
  - High humidity may affect the measurement.
  - For a 5 L air sample, working range of the method was determined to be 100–2600 mg/m^3.

    (1 ppm tetrahydrofuran in air = 2.95 mg/m^3 at NTP)

REFERENCE

National Institute for Occupational Safety and Health. 1984. *NIUOSH Manual of Analytical Methods*, 3rd edn. Cincinnati, OH: National Institute for Occupational Safety and Health.

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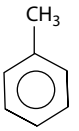
132 Toluene

Synonyms: methylbenzene, phenylmethane; formula: C_7H_8; structure:



MW 92.15; CAS [108-88-3]; occurs in gasoline, petroleum solvents, and coal-tar distillates; used as a solvent and in many organic syntheses; colorless liquid with a characteristic aromatic odor; boils at 110.7°C; freezes at −95°C; vapor pressure 22 Torr at 20°C; density 0.866 g/mL at 20°C; slightly soluble in water (0.63 g/L at 25°C); readily miscible with organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Purge and trap method; toluene bound onto the trap, thermally desorbed from the sorbent trap, and is swept by an inert gas onto a GC column, for separation from other volatile compounds; detected by PID, FID, or a mass spectrometer.
- Solid samples mixed with water or methanol; the aqueous extract or a portion of methanol extract spiked into water; subjected to the purge and trap concentration and analyzed as above.
- Alternatively, toluene thermally desorbed from the solid sample under the He purge (without any solvent treatment) and analyzed by GC or GC/MS as above.
  - Characteristic masses for GC/MS identification: 91, 92, 39, 65; peak ratios 91:92:39:65 = 100:73:20:14 (Hites, 1992).
  - Limit of detection: in the range 0.5 μg/L when detected by PID for a 5 mL sample volume (subject to matrix interference).
  - GC column: a nonpolar fused silica capillary column, such as DB-5, SPB-5, VOCOL, or equivalent.
  - Recommended surrogate/IS: toluene d_7 and fluorobenzene.
  - Samples collected in glass containers without headspace, refrigerated, and analyzed within 7 days; samples preserved with 1:1 HCl (0.2 mL acid/40 mL sample) may be analyzed in 14 days.
- Air drawn through a sorbent tube containing coconut shell charcoal (100 mg/50 mg); analyte desorbed into CS_2 over 30 min standing; analyzed by GC-FID (NIOSH Method 1501, 1984); recommended flow rate 200 mL/min; sample volume 20 L.
  - GC column: packed column 10% OV-275 on Chromosorb W-AW (100/120 mesh), Porapak P 50/80 mesh, or equivalent.
- Air drawn through a cartridge containing Tenax (∼2 g); cartridge heated under the He purge; toluene transported into a cold trap and then to the front of a GC column at −70°C; column heated; toluene determined by GC/MS (U.S. EPA, 1999. Method TO-1); recommended flow rate 100 mL/min; sample volume 10 L.

- Air passed through a cartridge containing carbon molecular sieve (~400 mg); cartridge heated at 350°C under the He purge; analyte carried into a cryogenic trap and flash evaporated onto a capillary column; determined by GC/MS (U.S. EPA Method TO-2); recommended flow rate 1 L/min; sample volume 100 L.
- Collected in a trap in liquid argon; the trap removed and heated; sample transferred to a precooled GC column for PID or FID detection (U.S. EPA Method TO-3).

(1 ppm toluene in air = 3.76 mg/m^3 at NTP)

REFERENCES

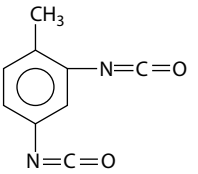
Hites, R.A. 1992. *Handbook of Mass Spectra of Environmental Contaminants*, 2nd edn. Boca Raton, FL: CRC Press.

National Institute for Occupational Safety and Health, 1984. *NIOSH Manual of Analytical Methods*, 3rd edn. Cincinnati, OH: National Institute for Occupational Safety and Health.

US EPA. 1999. *Method TO 1: Method for the Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Tenax Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS), Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.* Cincinnati, OH: Office of Research and Development, Center for Environmental Research Information.

133 Toluene-2,4-Diisocyanate

Synonyms: 2,4-diisocyanatotoluene, TDI, isocyanic acid 4-methyl-*m*-phenylene ester; formula: $CH_3C_6H_3(NCO)_2$; structure:



MW 174.16; CAS [584-84-9]; used in the production of urethane foams, elastomers, and coatings; also commercially available as a mixture of 2,4- and 2,6-isomers; colorless liquid or solid; turns dark on exposure to light; pungent fruity odor; boils at 238°C; melts at 20.5°C (80:20 mixture of the isomers melts at 13°C); density 1.22 g/mL; decomposes with water and alcohol; soluble in most organic solvents; highly toxic.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Sample extracted with methylene chloride; extract concentrated and analyzed by GC/MS.
  - The characteristic masses for compound identification: 174, 145, 173, 146, 132, and 91.
- Alternatively, sample extracted with toluene; extract treated with *N*-4-nitrobenzyl-*N*-propylamine (derivatizing agent) in toluene; TDI forms a urea derivative; the derivative extracted with acetonitrile and the extract solution then analyzed by HPLC-UV at 272 nm.
  - The method originally developed for air analysis (Tiesler and Eben, 1985); no data available on the precision and accuracy study for aqueous or solid matrices.
  - HPLC column and conditions: column packing: RP-8 or RP-18 (10 mm); temperature: ambient; mobile phase: acetonitrile–water; gradient program: from 30% acetonitrile to 60% in 15 min; 5 min isocratic; flow rate 1.5 mL/min.
  - For quantitation, prepare a calibration standard, plotting the concentration of urea derivative of each reference standard against peak areas.
  - Derivatizing agent prepared as follows: 50 g 4-nitrobenzyl chloride in 250 mL toluene heated under reflux; 36 g *n*-propylamine added dropwise in 30 min; refluxed for 5 h; solvent removed at 50°C on a rotary evaporator; residue treated with 80 mL water followed by a slow addition of 30 mL NaOH 40%; the alkaline solution is extracted with 100 mL toluene; the extract treated with 2 g charcoal and then filtered. The derivatizing agent prepared above is stable for 2–3 days. It may be converted into its hydrochloride as follows (which may be stable for several months):

Excess solvent and *n*-propylamine removed on a rotary evaporator; product dissolved in 50 mL acetone; 35 mL conc. HCl added; mixture dried at 50°C; hydrochloride repeatedly washed with acetone–toluene (1:1); the salt desiccated in the vacuum oven.

Hydrochloride may be converted back to the free amine-derivatizing agent prior to use. This may be done by dissolving the salt in water, then adding 1 N NaOH solution and extracting the free amine into toluene. The toluene phase is dried with Na_2SO_4 and then diluted to 250 mL. The concentration of this amine solution is 0.002 M (Soln. A). This may be 10-fold diluted to give 0.0002 M amine solution (Soln. B).

AIR ANALYSIS

- Air drawn through glass wool coated with *N*-[(4-nitropheny)methylpropylamine]; derivative desorbed into 2 mL methanol in ultrasonic bath; analyzed by HPLC using an UV detector at 254 nm (NIOSH Method 2535, 1987); recommended flow rate 0.5 L/min; sample volume 50 L.
  - Derivative is stable for 14 days if protected from light.
  - HPLC column: octadecylsilylated silica (5 μm).

  (1 ppm TDI = 7.12 mg/m^3 at NTP)

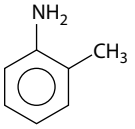
REFERENCES

National Institute for Occupational Safety and Health. 1987. *NIOSH Manual of Analytical Methods*, 3rd edition and updates. Cincinnati, OH: National Institute for Occupational Safety and Health.

Tiesler, A. and A. Eben. 1991. Hexamethylene diisocyanate: 2, 4- and 2, 6- Toluyelene diisocyanate. In *Analysis of Hazardous Substances in Air*, Vol. 1, eds. Kettrup, A. and D. Henschler, p. 75. Weihheim, Germany: VCH Verlagsgesellschaft mbH.

134 *o*-Toluidine

Synonyms: 2-methylaniline, 2-methylbenzenamine, 2-aminotoluene, *o*-tolylamine; formula: $C_7H_7NH_2$; structure:



MW 107.17; CAS [95-53-4]; used in the manufacture of various dyes and as an intermediate in rubber chemicals and pharmaceuticals; colorless liquid, becoming yellowish to reddish-brown on exposure to air or light; boils at 200°C; solidifies at −16°C; vapor pressure 0.1 Torr at 20°C; slightly soluble in water (1.5% at 20°C), readily miscible in organic solvents; carcinogenic and toxic at high doses (Patnaik, 2007).

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples made alkaline with NaOH to pH>12 and extracted with methylene chloride; analyte partitions into the organic phase; the organic extract concentrated and analyzed by GC-NPD or GC/MS.
  - GC column: packed −3% SP-2250 on Supelcoport, Chromosorb-103, or equivalent; capillary: fused silica capillary column such as DB-5, PTE-5, or other equivalent.
  - Characteristic masses for GC/MS identification: 107 and 106.
- Solid matrices mixed with anhydrous Na_2SO_4 followed by methylene chloride; sonicated; extract cleaned by acid-based partitioning and analyzed by GC-NPD, GC-FID, or GC/MS.
  - Aqueous and nonaqueous samples should be stored at 4°C, extracted within 7 days of collection, and analyzed within 40 days from extraction.

AIR ANALYSIS

- Analyte adsorbed over silica gel (150 mg/15 mg); desorbed into 95% ethanol in an ultrasonic bath and analyzed by GC-FID or GC-NPD (NIOSH Method 2002, 1985); recommended flow rate 200 mL/min; sample volume 20–30 L.
  - Adsorption efficiency of silica gel decreases under high humidity.
  - *o*-Toluidine is stable on silica gel at least for 1 week.
  - Sensitivity is much greater on GC-NPD.

  (1 ppm *o*-toluidine in air = −4.4 mg/m^3 at NTP)

REFERENCE

Patnaik, P. 2007. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 3rd edn. New York: John Wiley and Sons.

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135 1,1,1-Trichloroethane

Synonyms: methyl chloroform, strobane; formula: $C_2H_3Cl_3$; structure: $H_3C–CCl_3$; MW 133.40; CAS [71-55-6]; used as a cleaning solvent; colorless liquid with a mild chloroform-like odor; boils at 74°C; vapor pressure 100 Torr at 20°C; freezes at −32.5°C; density 1.34 g/mL at 20°C; very slightly soluble in water (~70 mg/L); soluble in organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Analyte in aqueous samples is extracted by the purge and trap method; volatile compounds thermally desorbed and swept onto a GC column for separation; detected by HECD, ECD, or MSD.
- Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water; subjected to the purge and trap concentration and analyzed as above.
  - Characteristic masses for GC/MS identification: 97, 99, 117, and 119.
  - Limit of detection: in the range 0.05 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: bromochloromethane and 1,2-dichloroethane d_4.
  - Samples collected in glass/plastic containers without headspace, refrigerated, and analyzed within 14 days.

See Chapter 32 for GC columns and conditions and a detailed discussion.

AIR ANALYSIS

- Suggested method: adsorbed over coconut charcoal (100 mg/50 mg); desorbed with CS_2 and analyzed by GC-FID; recommended flow rate 100 mL/min; sample volume 10 L; precision and accuracy of the method not established.
- Suggested method: adsorbed over carbon molecular sieve (~400 mg) in a cartridge; heated at 350°C under the He purge; transferred into a cryogenic trap and flash evaporated onto a capillary column GCVMS; recommended flow rate 2 L/min; sample volume 100 L; precision and accuracy of the method not known.
- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into cryogenically cooled trap attached to a GC column; the trap heated; the analyte separated on the column for detection by ECD or GC/MS (U.S. EPA, 1999. Method TO-14A).

REFERENCE

US EPA. 1999. *Method TO 14A: Determination of Volatile Organic Compounds (VOCs) Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography, Compendium Methods for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd edn. Cincinnati, OH: Office of Research and Development, Center for Environmental Research Information.

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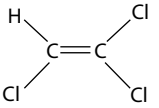
136 Trichloroethylene

Synonyms: trichloroethene, ethylene trichloride; formula C_2HCl_3; structure:



MW 131.38; CAS [79-01-6]; used in dry cleaning and degreasing; colorless liquid with chloroform-like odor; boils at 87°C; freezes at −85°C; vapor pressure 58 Torr at 20°C; density 1.46 g/mL at 20°C; very slightly soluble in water (about 1000 mg/L), miscible with organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples extracted by the purge and trap method; analyte thermally desorbed and swept onto a GC column for separation from other volatile compounds; detected by HECD, ECD, FID, or MSD.
- Soil, solid waste, or sludge mixed with water or methanol; the aqueous extract or a solution of methanol extract spiked into water; subjected to the purge and trap concentration and analyzed as above.
- Methanol extract may be directly injected for GC or GC/MS determination.
  - Characteristic masses for GC/MS identification: 95, 97, 130, and 132.
  - Limit of detection: in the range 0.1 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: 1,2-dichloroethane d_4 and 2-bromo-l-chloropropane.
  - Samples collected in glass/plastic containers without headspace, refrigerated, and analyzed within 14 days.

See Chapter 32 for GC columns and conditions and further discussion.

AIR ANALYSIS

- Adsorbed over coconut charcoal (100 mg/50 mg); desorbed with CS_2; and analyzed by GC-FID; recommended flow rate 100 mL/min; sample volume 5 L.
- Adsorbed over carbon molecular sieve (~400 mg) in a cartridge heated at 350°C under He purge; transferred into a cryogenic trap and flash evaporated onto a capillary column GC/MS (U.S. EPA, 1999. Method TO-2); 1 L/min recommended flow rate; sample volume 100 L.
- Collected in a trap in liquid argon; the trap removed and heated; sample transferred to a precooled GC column for ECD or FID detection (U.S. EPA, 1999. Method TO-3).
- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into a cryogenically cooled trap attached to a GC column; the trap heated; the analyte separated on the column for detection by ECD or GC/MS (U.S. EPA, 1999. Method TO-14A).

(1 ppm trichloroethylene in air = 5.36 mg/m^3 at NTP)

REFERENCES

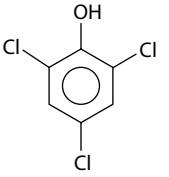
US EPA. 1999. *Method TO 2: Method for Determination of Volatile Organic Compounds (VOCs) in Ambient Air by Carbon Molecular Sieve Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS), Compendium Methods for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd edn. Cincinnati, OH: Office of Research and Development, Center for Environmental Research Information.

US EPA. 1999. *Method TO 3: Determination of Volatile Organic Compounds in Ambient Air Using Cryogenic Preconcentration Techniques and Gas Chromatography with Flame Ionization and Electron Capture Detection, Compendium Methods for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd edn. Cincinnati, OH: Office of Research and Development, Center for Environmental Research Information.

US EPA. 1999. *Method TO 14A: Determination of Volatile Organic Compounds (VOCs) Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography, Compendium Methods for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd edn. Cincinnati, OH: Center for Environmental Research Information.

137 2,4,6-Trichlorophenol

Formula: $C_6H_2Cl_3OH$; structure:



MW 197.46; CAS [88-06-2]; crystalline solid with strong phenolic odor; melts at 69°C; boils at 246°C; insoluble in water; soluble in most organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Aqueous samples pH adjusted to below 2; extracted with methylene chloride; extract concentrated and analyzed by GC-FID or GC/MS.
  - Alternatively, extract exchanged into 2-propanol; derivatized with pentafluorobenzyl bromide, and determined by GC-ECD.
  - Aqueous samples may be analyzed by HPLC on an underivatized polystyrene–divinylbenzene column such as Poly-RP CO (Alltech, 1995) or a C-18 reverse-phase column; gradient: acetonitrile and 0.01 M K_3PO_4 at pH 7 (55:45) and the analyte detected by UV at 254 nm.
- Soil, solid waste, and sludge extracted with methylene chloride by sonication, Soxhlet, or supercritical fluid extraction; extract may be acid washed, concentrated, and analyzed by GC-FID, GC-ECD, or GC/MS as above.
  - Characteristic masses for GC/MS determination: 196, 198, and 200 (electron impact ionization); 197, 199, and 201 (chemical ionization).
  - Limit of detection: in the range 5–10 μg/L on FID or GC/MS and below 1 μg/L on ECD (for aqueous samples concentrated by 1000 times).
  - Recommended surrogate/IS: pentafluorophenol and 2-perfluoromethyl phenol.
  - Sample collected in glass containers, refrigerated, extracted within 7 days of collection, and analyzed within 40 days of extraction.

See Chapter 49 for GC columns and conditions.

AIR ANALYSIS

Not likely to occur in ambient air in the vapor state; the vapor pressure is too low.

Recommended method: airborne particles collected on a sorbent cartridge containing polyurethane foam; deposited particles extracted with 5% diethyl ether in hexane; extract analyzed by GC-ECD; recommended airflow 5 L/min; sample volume 1000 L.

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138 Vinyl Chloride

Synonyms: chloroethene, monochloroethylene; formula: $CH_2 = CHCl$; MW 62.50; CAS [75-01-4]; used as a monomer to make PVC resins and plastics; a colorless gas; liquefies at −13.4°C; slightly soluble in water; miscible in organic solvents.

ANALYSIS OF AQUEOUS SAMPLES

- Aqueous samples extracted by the purge and trap method; analyte thermally desorbed and swept onto a GC column for separation; detected by HECD, ECD, and MSD.
  - Characteristic masses for GC/MS identification: 62 and 64.
  - Limit of detection: in the range of 0.1 μg/L when detected by HECD for a 5 mL sample aliquot (subject to matrix interference).
  - Recommended surrogate/IS: bromochloromethane and 1,2-dichloroethane d_4.
  - Samples collected in glass/plastic containers without headspace, refrigerated, and analyzed within 14 days.

See Chapter 32 for GC columns and conditions and further discussion.

AIR ANALYSIS

- Adsorbed over carbon molecular sieve (~400 mg) in cartridge; heated at 350°C under the He purge; transferred into a cryogenic trap and flash evaporated onto a capillary column GC/MS; recommended flow rate 100 mL/min; sample volume 10 L (U.S. EPA, 1999. Method TO-2).
- Collected in a trap in liquid argon; the trap removed and heated; sample transferred to a precooled GC column for ECD detection (U.S. EPA, 1999. Method TO-3).
- Collected in a SUMMA passivated canister under pressure using an additional pump or at subatmospheric pressure by initially evacuating the canister; the air transferred into a cryogenically cooled trap attached to a GC column; the trap heated; the analyte separated on the column for detection by ECD or GC/MS (U.S. EPA, 1999. Method TO-14A).

(1 ppm vinyl chloride in air = 2.5 mg/m^3 at NTP).

REFERENCES

US EPA. 1999. *Method TO 2*: *Method for Determination of Volatile Organic Compounds (VOCs) in Ambient Air by Carbon Molecular Sieve Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS), Compendium Methods for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd edn. Cincinnati, OH: Office of Research and Development, Center for Environmental Research Information.

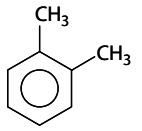
US EPA. 1999. *Method TO 3: Determination of Volatile Organic Compounds in Ambient Air Using Cryogenic Preconcentration Techniques and Gas Chromatography with Flame Ionization and Electron Capture Detection, Compendium Methods for the Determination of Toxic Organic*

Compounds in Ambient Air, 2nd edn. Cincinnati, OH: Office of Research and Development, Center for Environmental Research Information.

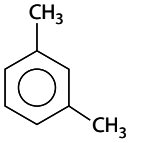
US EPA, 1999. *Method TO 14A : Determination of Volatile Organic Compounds (VOCs) Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography, Compendium Methods for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd edn. Cincinnati, Ohio: Center for Environmental Research Information.

139 Xylene

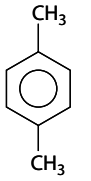
Synonym: dimethyl benzene; formula: C_8H_{10}; structures: xylene occurs in three isomeric forms as *ortho*-, *meta*-, and *para*-isomers.



(*o*-Xylene)



(*m*-Xylene)



(*p*-Xylene)

MW 106.18; CAS [1330-20-7]; [95-47-6] for *o*-xylene, [108-38-3] for *m*-xylene and [106-42-3] for *p*-xylene; used as a solvent and in the manufacture of dyes and drugs; occurs in gasoline and petroleum solvents; colorless liquid with characteristic odor; boiling point for *o*-, *m*-, and *p*-isomers 144.4°C, 139.1°C, and 138.4°C, respectively; their vapor pressures at 20°C are 6.7, 8.4, and 8.8 Torr, respectively; density 0.880, 0.864, and 0.861 g/mL, respectively; practically insoluble in water; readily miscible with organic solvents.

ANALYSIS OF AQUEOUS AND NONAQUEOUS SAMPLES

- Purge and trap extraction method; xylene thermally desorbed from the sorbent trap and backflushed with an inert gas onto a GC column for separation from other volatile compounds; detected by PID, FID, or a mass spectrometer.
- Solid samples mixed with methanol; an aliquot of methanol extract spiked into a measured volume of water in a purging vessel, subjected to purge and trap concentration, and analyzed as above.
- Alternatively, xylene thermally desorbed out from the solid matrix under the He purge (without any solvent treatment) and analyzed by GC or GC/MS.
  - The characteristic masses for GC/MS identification: 106 and 91; all three isomers of xylene and ethyl benzene produce the same characteristic masses. These isomers and ethyl benzene should, therefore, be identified from their retention times, which are in the following order of elution:

$$\text{ethyl benzene} < p\text{-xylene} \sim m\text{-xylene} < o\text{-xylene}$$

In most columns, two peaks will be observed, coeluting *m*- and *p*-xylene, followed by *o*-xylene; *m*- and *p*-isomers mostly coelute. Separation of these two isomers may be achieved to some degree by using a narrow bore capillary column of 100 m length. Under such conditions, *p*-isomer should elute before *m*-xylene; *o*-xylene shows a longer retention time and may be readily separated from its other isomers.

- GC column: a fused silica capillary column such as DB-5, DB-624, VOCOL, or equivalent.
- Recommended surrogate/IS: ethyl benzene-d_5 (*m/z* 111) and 1,4-difluoro-benzene (*w/z* 114,63,88).
- Samples collected in glass containers without headspace, refrigerated, and analyzed within 7 days. Samples preserved with 1:1 HCl (a few drops/40 mL sample) may be analyzed in 14 days.

AIR ANALYSIS

- Air drawn through a sorbent tube packed with coconut shell charcoal (100 mg/50 mg); xylene desorbed into CS_2 (more than 30 min standing); CS_2 extract analyzed by GC-FID (NIOSH method 1501, 1984); recommended airflow rate 100 mL/min; sample volume 20 L.
  - GC column: 10% OV-275 on 100/120 mesh Chromosorb W-AW or equivalent. Xylene elutes as two peaks, *p*- and *m*-xylene coeluting, followed by *o*-xylene.
- Air drawn through a cartridge packed with Tenax (2 g); cartridge heated under the He purge; analyte transported into a cold trap and then to the front of a GC column at −70°C; column temperature programmed; xylene determined by GC/MS (U.S. EPA method TO-1); recommended flow rate 100 mL/min; sample volume 10 L.
- Air drawn through a cartridge packed with carbon molecular sieve (400 mg); cartridge heated at 350°C under the He purge; analyte transported into a cryogenic trap; flash evaporated onto a capillary column; determined by GC/MS (U.S. EPA method TO-2); recommended flow rate 2 L/min; sample volume 100 L.
- Air collected in a SUMMA passivated stainless steel canister either by pressurizing the canister using a sample pump or by repeated preevacuation; canister then attached to an analytical system; air sample collected transferred to a cryogenically cooled trap; cryogen removed and temperature raised; analyte revolatilized; separated on a GC column; determined by PID, FID, or a mass spectrometer (U.S. EPA method TO-14).

(1 ppm xylene in air = 4.34 mg/m^3 at NTP)

Appendix A: Some Common QC Formulas and Statistics

MEASUREMENT OF PRECISION

Standard Deviation

$$s\sqrt{\sum x^2 - \frac{(\sum x)^2/n}{n-1}}$$

where

s is the standard deviation
$\sum x^2$ is the sum of squares of individual measurements
$\sum x$ is the sum of individual measurements
n is the number of individual measurements

An estimate of standard deviation can be calculated from the following formula:

$$s = \sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}}$$

Relative Standard Deviation (RSD)

(Also known as the coefficient of variance)

$$\text{RSD} = \frac{s}{x} \times 100\%$$

where x– is the average of test results.

Standard Error of Mean (M)

$$M = \frac{s}{\sqrt{n}}$$

where n is the number of measurements.

Relative Percent Difference (RPD)

$$\text{RPD} = \frac{\text{Difference of two measurements}}{\text{Average of two measurements}} \times 100$$

MEASUREMENT OF LINEARITY OF DATA POINTS

Correlation Coefficient (γ)

The correlation coefficient (γ) is a measure of the linear relationship between two sets of data. It can attain a value that may vary between 0 and ± 1. A value of $+1$ (or -1, when the slope is negative) indicates the maximum possible linearity; on the other hand, a zero γ indicates that there is absolutely no link between the data. In environmental analysis, especially in spectrophotometric methods, γ is calculated to determine the linearity of the standard calibration curve. γ may be calculated from one of the following equations.

$$\gamma = \frac{s_x}{s_y} \times b$$

where

s_x and s_y are the standard deviations in x and y sets of data, respectively
b is the slope of the line

The above relationship, however, is susceptible to error, because b can change depending on how we manipulate to construct the line of best fit. The correlation coefficient, however, can be best determined from one of the following two equations:

$$\gamma = \frac{\Sigma xy - \left(\Sigma x \Sigma y / n\right)}{\sqrt{\left[\Sigma x^2 - \frac{(\Sigma x)^2}{n}\right]\left[\Sigma y^2 - \frac{(\Sigma y)^2}{n}\right]}}$$

or

$$\gamma = \frac{\Sigma xy - n\overline{xy}}{\sqrt{\left[\Sigma x^2 - n(\overline{x})^2\right] \quad \left[\Sigma y^2 - n(\overline{y})^2\right]}}$$

EXAMPLE

Determine the correlation coefficient of the standard calibration curve for residual chlorine from the following sets of data.

Concentration (mg/L) (x)	Absorbance (y)
0.10	0.023
0.15	0.030
0.30	0.066
0.35	0.075
0.45	0.094
0.55	0.112

$$\gamma = \frac{\Sigma xy - n\overline{x}\overline{y}}{\sqrt{[\Sigma x^2 - n\overline{x}^2] \quad [\Sigma y^2 - n\overline{y}^2]}}$$

$$\Sigma xy = 0.3167, \quad n = 6$$

$$\begin{array}{ll} \overline{x} = 0.3167 & \overline{y} = 0.0667 \\ (\overline{x})^2 = 0.1003 & (\overline{y})^2 = 0.00444 \\ \Sigma x^2 = 0.75 & \Sigma y^2 = 0.0328 \end{array}$$

$$\begin{aligned} \gamma &= \frac{0.1567 - 0.1267}{\sqrt{(0.7500 - 0.6017)(0.03828 - 0.0267)}} \\ &= \frac{0.0300}{\sqrt{(0.1483)(0.0062)}} \\ &= \frac{0.0300}{0.0303} \\ &= 0.9901 \end{aligned}$$

The above value of γ is very close to +1.0000. Therefore, the standard calibration curve is highly linear.

MEASUREMENT OF ACCURACY

Percent Spike Recovery by U.S. EPA Formula

$$\%\ \text{Recovery} = \frac{X_s - X_u}{K} \times 100\%$$

where

X_s is the measured value for the spiked sample
X_u is the measured value for the unspiked sample adjusted for the dilution of the spike
K is the known value of the spike in the sample.

(This is a U.S. EPA percent spike recovery formula.)

Percent Spike Recovery by Alternate Method

$$\%\ \text{Recovery} = \frac{\text{Measured concentration}}{\text{True concentration}} \times 100\%$$

The above formula may be directly used without any volume correction, if the volume of spike added is very small, that is, <1% sample volume. However, if the volume of the spike solution added to the sample is large (>5% of the volume of the sample), the true (or expected) concentration in the above formula may be determined as follows:

$$\text{True concentration} = \frac{(C_u \times V_u)}{(V_u + V_s)} + \frac{(C_s \times V_s)}{(V_u + V_s)}$$

where

C_u is the measured concentration of the analyte in the sample
C_s is the concentration of the analyte in the spike standard
V_u is the volume of the sample
V_s is the volume of the spike standard added

(See Chapter 2 for solved examples.)

METHOD DETECTION LIMITS FOR ORGANIC POLLUTANTS IN AQUEOUS SAMPLES

Method Detection Limit (MDL)

$$\text{MDL} = t \times s$$

where

t is the students' t value for $(n - 1)$ measurements
s is the standard deviation of the replicate analyses

Note that the t-statistics should be followed when the sample size is small, that is, <30. In MDL measurements, the number of replicate analyses is well below 30, generally 7. For example, if the number of replicate analyses is 7, then the degrees of freedom, that is, the $(n - 1)$ is 6, and, therefore, the t value for 6 should be used in the above calculation. MDL must be determined at the 99% confidence level. When analyses are performed by GC or GC/MS methods, the concentrations of the analytes to be spiked into the seven aliquots of the reagent grade water for the MDL determination should be either at the levels of their IDL (instrument detection limit) or five times the background noise levels (the noise backgrounds) at or near their respective retention times.

t Values at the 99% Confidence Level

Number of Replicate Measurements	Degrees of Freedom $(n - 1)$	t Values
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457

Appendix B: Sample Containers, Preservations, and Holding Times

Analyte	Container	Preservation	Maximum Holding Time
		Inorganics and Microbial Tests	
Acidity	P, G	Cool, 4°C	14 days
Alkalinity	P, G	Cool, 4°C	14 days
Bacterias, coliform (total and fecal)	P, G	Cool, 4°C; add 0.008% $Na_2S_2O_3$ if residual chlorine is present	6 h
Biochemical oxygen demand	P, G	Cool, 4°C	48 h
Bromide	P, G	None required	28 days
Chloride	P, G	None required	28 days
Chlorine, residual	P, G	None required	Analyze immediately
Chemical oxygen demand	P, G	Cool, 4°C, H_2SO_4 to pH < 2	28 days
Color	P, G	Cool, 4°C	48 h
Cyanide	P, G	Cool, 4°C, pH > 12, 0.6 g ascorbic acid	14 days
Fluoride	P	None required	28 days
Hardness	P, G	pH < 2 with HNO_3 or H_2SO_4	6 months
Iodine	P, G	None required	Analyze immediately
Kjeldahl nitrogen	P, G	Cool, 4°C, pH < 2 with H_2SO_4	28 days
Metals (except chromium-VI, boron, and mercury)	P, G	HNO_3 to pH < 2	6 months
Chromium-VI	P, G	Cool, 4°C	24 h
Mercury	P, G	HNO_3 to pH < 2	28 days
Boron	P	HNO_3 to pH < 2	28 days
Nitrate	P, G	Cool, 4°C, H_2SO_4 to pH < 2	28 days
Nitrite	P, G	Cool, 4°C	48 h
Odor	G	None required	Analyze immediately
Oil and grease	G	Cool, 4°C, H_2SO_4 or HCl to pH < 2	28 days
Oxygen, dissolved	G (BOD bottle)	None required	Analyze immediately
pH	P, G	None required	Analyze immediately
Phenolics	G	Cool 4°C, H_2SO_4 to pH < 2	28 days
Phosphorus			
Elemental	G	Cool, 4°C	48 h
Orthophosphate	P, G	Cool, 4°C	48 h
Total	P, G	Cool, 4°C, H_2SO_4 to pH < 2	28 days

(*Continued*)

Analyte	Container	Preservation	Maximum Holding Time
Residue			
Total	P, G	Cool, 4°C	7 days
Filterable	P, G	Cool, 4°C	7 days
Nonfilterable (TSS)	P, G	Cool, 4°C	7 days
Settleable	P, G	Cool, 4°C	48 h
Volatile	P, G	Cool, 4°C	7 days
Silica	P	Cool, 4°C	28 days
Specific conductance	P, G	Cool, 4°C	28 days
Sulfate	P, G	Cool, 4°C	28 days
Sulfide	P, G	Cool, 4°C, zinc acetate plus NaOH to pH > 9	7 days
Sulfite	P, G	None required	Analyze immediately
Surfactants	P, G	Cool, 4°C	48 h
Taste	G	Cool, 4°C	24 h
Temperature	P, G	None required	Analyze
Total organic carbon	G	Cool, 4°C, HCl or H_2SO_4 to pH < 2	28 days
Total organic halogen	G (amber bottles)	Cool, 4°C, store in dark, HNO_3 to pH < 2, add Na_2SO_3 if residual chlorine present	14 days
Turbidity	P, G	Cool, 4°C	48 h
		Organics Tests	
Purgeable halocarbons	G (Teflon-lined septum)	Cool, 4°C, no headspace (add 0.008% $Na_2S_2O_3$ if residual chlorine is present)	14 days
Purgeable aromatics	G (Teflon-lined septum)	Cool, 4°C, no headspace (add 0.008% $Na_2S_2O_3$ if residual chlorine is present), HCl to pH < 2	14 days
Pesticides, chlorinated	G (Teflon-lined cap)	Cool, 4°C, pH 5–9	7 days until extraction; 40 days after extraction
PCBs	G (Teflon-lined cap)	Cool, 4 °/C	7 days until extraction; 40 days after extraction
Phthalate esters	G (Teflon-lined cap)	Cool, 4°/C	7 days until extraction; 40 days after extraction
Nitroaromatics	G (Teflon-lined cap)	Cool, 4°C (add 0.008% $Na_2S_2O_3$, if residual chlorine present), store in dark	7 days until extraction; 40 days after extraction
Nitrosamines	G (Teflon-lined cap)	Cool, 4°C (add 0.008% $Na_2S_2O_3$, if residual chlorine present), store in dark	7 days until extraction; 40 days after extraction
Polynuclear aromatic hydrocarbons	G (Teflon-lined cap)	Cool, 4°C (add 0.008% $Na_2S_2O_3$, if residual chlorine present), store in dark	7 days until extraction; 40 days after extraction

(*Continued*)

Analyte	Container	Preservation	Maximum Holding Time
Haloethers	G (Teflon-lined cap)	Cool, 4°C (add 0.008% $Na_2S_2O_3$, if residual chlorine present)	7 days until extraction; 40 days after extraction
Phenols	G (Teflon-lined cap)	Cool, 4°C (add 0.008% $Na_2S_2O_3$, if residual chlorine present)	7 days until extraction; 40 days after extraction
Dioxins and dibenzofurans	G (Teflon-lined cap)	Cool, 4°C (add 0.008% $Na_2S_2O_3$, if residual chlorine present)	7 days until extraction; 40 days after extraction

Note: P, polyethylene; G, glass. If there is no residual chlorine in the sample, the addition of $Na_2S_2O_3$ may be omitted.

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Appendix C: Preparation of Molar and Normal Solutions of Some Common Reagents

Concentrations of reagents and titrants in wet analysis are commonly expressed in terms of molarity (M) or normality (N). One mole (molecular or formula weight expressed in grams) of a substance dissolved in 1 L of its aqueous solution produces 1 M.

$$\text{Molarity, M} = \frac{\text{Number of moles of the solute (or reagent)}}{\text{Liter of its solution}}$$

For example, 158.10 g sodium thiosulfate ($Na_2S_2O_3$) in 1 L of its solution is 1 M; or 1.581 g $Na_2S_2O_3$ per liter is 0.01 M. The amount of a substance to be dissolved in water and made up to any specific volume of its solution for obtaining a concentration of any specific molarity is determined as follows.

EXAMPLE

How many grams of potassium hydrogen phthalate ($KHC_8H_4O_4$) must be added to water to produce 250 mL of 0.015 M solution?

$$\text{M} = 0.015, \text{volume of solution} = 0.250\ \text{L}$$

Thus,

$$0.015 = \frac{\text{Number of moles of } KHC_8H_4O_4}{0.250}$$

Therefore, the number of moles of $KHC_8H_4O_4 = 0.015 \times 0.250 = 0.00375$ mol, which is equal to

$$0.00375\ \text{mol}\ KHC_8H_4O_4 \times \frac{204.23\ \text{g}\ KHC_8H_4O_4}{1\ \text{mol}\ KHC_8H_4O_4} = 0.766\ \text{g}\ KHC_8H_4O_4$$

That is, 0.766 g $KHC_8H_4O_4$ is to be dissolved in water to a volume of 250 mL to produce 0.015 M solution.

Normality (N), on the other hand, is the number of gram equivalent of a substance per liter of solution; or the number of milligram equivalent per mL of solution. Gram equivalent is the equivalent weight of the compound expressed in grams. Often, normality of a reagent is the same as its molarity. In addition, the normality of a substance may differ widely from its molarity, depending on the reactions. Such a wide difference may conspicuously be noted, especially in the case of oxidizing and reducing agents in redox reactions. In such reactions, equivalent weight is determined from the change in the oxidation number of the element during titration. The molarity (gram molecular weights/liter) and normality (gram equivalent weight/liter) of some common reagents in wet analysis are presented below.

Compound	Formula	1.00 M (g/L)	1.00 N[a] (g/L)
Arsenic trioxide	As_2O_3	197.85	49.455
Barium hydroxide	$Ba(OH)_2$	171.26	85.68
Ferrous ammonium sulfate (hexahydrate)	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	392.14	–
Hydrochloric acid	HCl	36.46	36.46
Iodine	I_2	253.80	126.90
Mercuric nitrate	$Hg(NO_3)_2$	324.61	162.30
Nitric acid	HNO_3	63.01	63.01
Potassium biiodate	$KH(IO_3)_2$	389.92	32.49
Potassium bromate	$KBrO_3$	163.01	27.17
Potassium chlorate	$KClO_3$	122.55	20.4
Potassium chloride	KCl	74.56	74.56
Potassium dichromate	$K_2Cr_2O_7$	294.19	49.04
Potassium hydrogen phthalate	$KHC_8H_4O_4$	204.23	204.23
Potassium hydroxide	KOH	56.11	56.11
Potassium iodate	KIO_3	214.00	42.8[b]
Potassium oxalate	$K_2C_2O_4$	166.19	83.09
Potassium permanganate	$KMnO_4$	158.04	31.61[c]
Potassium persulfate	$K_2S_2O_8$	270.33	135.16
Silver nitrate	$AgNO_3$	169.87	169.87
Sodium carbonate	Na_2CO_3	105.99	53.00
Sodium chloride	NaCl	58.44	58.44
Sodium thiosulfate	$Na_2S_2O_3$	158.10	158.10
Sulfuric acid	H_2SO_4	98.08	49.04

[a] The equivalent weight is highly reaction specific, which can change with pH and redox conditions.

[b] Under strong acid conditions, the reaction is $IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$.

[c] Equivalent weight of $KMnO_4$ could be 52.68, when the redox reaction is $MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_{2(S)} + 4OH^-$.

Appendix D: Characteristic Masses of Miscellaneous Organic Pollutants (Not Listed in Text) for GC/MS Identification*

CAS No.	Compounds	Primary Ion (*m/z*)	Secondary Ions (*m/z*)
75-86-5	Acetone cyanohydrin	43	58, 27
123-54-6	Acetylacetone	43	85, 100
260-94-6	Acridine	179	89, 178, 180
79-06-1	Acrylamide	44	71, 55, 27
15972-60-8	Alachlor	45	160, 188, 237, 146
116-06-3	Aldicarb	58	86, 41, 89, 144, 100
2032-59-9	Aminocarb	151	150, 136, 208
834-12-8	Ametryne	227	212, 58, 170, 185, 98
61-82-5	Amitrole	84	29, 57, 44
84-65-1	Anthraquinone	208	108, 152, 76, 126
1912-24-9	Atrazine	200	58, 215, 173, 202, 69
103-33-3	Azobenzene	77	51, 182, 105, 152
275-51-4	Azulene	128	51, 102
101-27-9	Barban	222	87, 51, 104, 143, 257
22781-23-3	Bendiocarb	151	166, 126, 58, 223
1861-40-1	Benfluralin	292	41, 264, 160, 105, 206
65-85-0	Benzoic acid	105	122, 77, 51
100-47-0	Benzonitrile	103	76, 50, 104
119-61-9	Benzophenone	105	77, 182, 51
98-88-4	Benzoyl chloride	105	77, 51, 50
100-44-7	Benzyl chloride	91	126, 65, 92
17804-35-2	Benomyl	191	159, 105, 40, 132, 146
314-40-9	Bromacil	205	207, 41, 69, 163, 233, 262
90-11-9	1-Bromonaphthalene	206	127, 208, 126
18181-80-1	Bromopropylate	43	75, 185, 104, 155, 341
23184-66-9	Butachlor	57	176, 160, 188, 237
123-86-4	Butyl acetate	43	86, 73
75-64-9	*tert*-Butylamine	58	41, 42
111-76-2	Butyl cellosolve	57	45, 87, 41, 75
15271-41-7	Butyllate	58	39, 184, 148, 118, 96
76-22-2	Camphor	95	81, 152, 108, 69
63-25-2	Carbaryl	144	115, 116, 145, 201
86-74-8	9H-Carbazole	167	166, 139, 168, 44
1563-66-2	Carbofuran	164	149, 122, 123, 201

(*Continued*)

* Electron impact ionization at 70 V (nominal).

CAS No.	Compounds	Primary Ion (*m/z*)	Secondary Ions (*m/z*)
118-75-2	Chloranil	87	246, 209, 244, 211, 218
78-95-5	Chloroacetone	49	42, 92, 77, 51
510-15-6	Chlorobenzilate	251	139, 253, 111, 141
118-91-2	2-Chlorobenzoic acid	139	156, 111, 75, 50, 121
563-47-3	2-Chloro-3-methylpropene	55	39, 90, 54, 75
90-13-1	Chloronaphthalene	162	127, 164, 63
1897-45-6	Chlorothalonil	266	264, 268, 109, 124
191-07-1	Coronene	300	150, 149, 301
123-73-9	Crotonaldehyde	70	41, 39, 69
98-82-8	Cumene	105	120, 77, 51, 79
110-82-7	Cyclohexane	56	84, 41, 55, 69
108-93-0	Cyclohexanol	57	44, 67, 82
108-91-8	Cyclohexylamine	56	43, 99, 70
94-75-7	2,4-D	162	220, 164, 133, 175, 63
94-82-6	2,4-DB	162	164, 87, 63
96-12-8	DBCP	157	75, 155, 77, 49, 62
1861-32-1	DCPA	301	299, 303, 332, 221
75-99-0	Dalapon	28	36, 62, 43, 97, 106
2303-16-4	Diallate	86	234, 70, 128, 109, 58
1918-00-9	Dicamba	173	220, 191, 97, 149, 175
117-80-6	Dichlone	191	226, 163, 228, 135, 99
91-94-1	3,3′-Dichlorobenzidine	252	254, 126, 154
75-71-8	Dichlorodifluoromethane	85	87, 50, 101
120-36-5	Dichlorprop	162	164, 234, 189, 98
542-75-6	1,3-Dichloropropene	75	39, 77, 49, 110, 112
97-23-4	Dichlorophene	128	141, 268, 215, 152
115-32-2	Dicofol	139	111, 141, 250, 75
111-42-2	Diethanolamine	74	30, 56, 42
109-89-7	Diethylamine	30	27, 58, 44, 73
88-85-7	Dinoseb	211	163, 147, 117, 240
122-39-4	Diphenylamine	169	168, 77, 51
330-54-1	Diuron	72	232, 234, 44
145-73-3	Endothall	68	100, 69, 82, 140
75-08-1	Ethanethiol	62	47, 29, 34, 45
100-41-4	Ethylbenzene	91	106, 51, 39
110-77-0	2-(Ethylthio)ethanol	75	47, 106, 45, 61
101-42-8	Fenuron	72	164, 44, 70, 77
14484-64-1	Ferbam	88	296, 44, 175, 120, 416
944-22-9	Fonofos	109	137, 246, 110, 81
98-01-1	Furfural	39	96, 95, 38, 29
118-74-1	Hexachlorobenzene	284	286, 282, 142, 249
67-72-1	Hexachloroethane	201	117, 119, 203, 166
110-19-0	Isobutyl acetate	43	56, 73
314-42-1	Isocil	204	206, 163, 161, 120, 70, 246
465-73-6	Isodrin	193	195, 66, 263, 147
148-24-3	Isoquinoline	129	102, 51, 128
566-61-6	Isothiocyanatomethane	73	72, 45, 70
143-50-0	Kepone	272	274, 270, 237, 355
330-55-2	Linuron	61	46, 248, 160
2032-65-7	Methiocarb	168	153, 109, 225, 91
16752-77-5	Methomyl	54	105, 87, 42, 28

(*Continued*)

CAS No.	Compounds	Primary Ion (*m/z*)	Secondary Ions (*m/z*)
99-76-3	Methylparaben	121	152, 93, 65
51218-45-2	Metolachlor	162	45, 238, 146, 91
21087-64-9	Metribuzin	198	41, 57, 103, 74, 144, 214
315-18-4	Mexacarbate	165	150, 134, 222
2385-85-5	Mirex	272	274, 270, 237, 332
150-68-5	Monuron	72	198, 40, 28
110-91-8	Morpholine	57	29, 87, 56, 86
134-32-7	1-Naphthylamine	143	115, 116, 89, 63
91-59-8	2-Naphthylamine	143	115, 116, 89, 63
555-37-3	Neburon	40	114, 187, 274, 276
54-11-5	Nicotine	84	162, 133, 161
1836-75-5	Nitrofen	283	285, 202, 139, 162
930-55-2	*N*-Nitrosopyrrolidine	41	100, 42, 69, 43
25154-52-3	Nonyl phenol	149	107, 121, 55, 77
23135-22-0	Oxamyl	72	44, 162, 115, 88, 145
101-84-8	Phenyl ether	170	141, 77, 51
84-62-8	Phenyl phthalate	65	44, 66, 91, 105, 120
1918-02-1	Picloram	196	198, 161, 163, 86, 240
2631-37-0	Promecarb	135	150, 91, 58
7287-19-6	Prometryne	241	58, 184, 226, 106
1918-16-7	Propachlor	120	77, 93, 176, 211
709-98-8	Propanil	161	163, 57, 29, 217
122-42-9	Propham	43	93, 179, 137, 120
114-26-1	Propoxur	110	152, 81, 58, 209
91-22-5	Quinoline	129	102, 51, 128
83-79-4	Rotenone	192	394, 191, 177, 28
93-72-1	Silvex	196	198, 97, 270, 268, 167
1982-49-6	Siduron	93	55, 56, 94, 232
122-34-9	Simazine	44	201, 186, 68, 173
1014-70-6	Simetryne	213	68, 170, 155, 71
57-24-9	Strychnine	334	335, 120, 36, 162
100-42-5	Styrene	104	103, 78, 51, 77
95-06-7	Sulfallate	188	72, 88, 60, 148, 223
93-76-5	2,4,5-T	196	198, 254, 256, 167, 97
5902-51-2	Terbacil	161	160, 162, 56, 116, 216
53555-64-9	Tetrachloronaphthalene	266	264, 268, 194
119-64-2	Tetralin	104	132, 91, 41
137-26-8	Thiram	88	120, 240, 44
119-93-7	2-Tolidine	212	106, 196, 180
76-03-9	Trichloroacetic acid	44	83, 85, 36, 117
87-61-6	Trichlorobenzene	180	182, 145, 184, 109
75-69-4	Trichlorofluoromethane	101	103, 66, 105, 152
55720-37-1	Trichloronaphthalene	230	232, 160, 234
102-71-6	Triethanolamine	118	56, 45, 42
121-44-8	Triethylamine	86	30, 58, 101
1582-09-8	Trifluralin	306	264, 43, 290, 335
75-50-3	Trimethylamine	58	59, 42, 30
51-79-6	Urethan	31	44, 45, 62, 74
108-05-4	Vinyl acetate	43	86, 42, 44
1330-20-7	Xylene	91	106, 105, 77, 51

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Appendix E: Volatility of Some Additional Organic Substances (Not Listed in Text) for Purge and Trap Analysis

Volatility data are presented in the following table for some additional organic compounds. These substances may be analyzed in aqueous samples using the purge and trap technique. For the purge and trap extraction of an organic compound from an aqueous matrix, the compound should ideally have a high vapor pressure, low boiling point, and low solubility in water. An inert gas or a gas that does not react with the analyte is bubbled through a measured volume of sample aliquot in a purging vessel. The compound is swept onto a sorbent trap, filled with tenax, activated charcoal, and silica gel (or equivalent materials), where it is adsorbed. It is then thermally desorbed from the trap and then transported under the flow of a carrier gas onto a temperature programmed GC column for separation from other volatile substances. The compounds are detected either by a mass spectrometer or by a FID. Alternatively, halogenated organics may be determined by an ECD or another halogen-specific detector.

CAS No.	Compound	Boiling Point (°C)	Vapor Pressure at 20°C (Torr)
67-64-1	Acetone[a]	56.2	105[c] at 8°C
506-96-7	Acetyl bromide	76.0	80[c]
75-36-5	Acetyl chloride	50.9	175[c]
107-18-6	Allyl alcohol[a]	97.1	10 at 10°C
300-57-2	Allyl benzene[b]	156	5[c]
106-95-6	Allyl bromide	70	150[c]
107-05-1	Allyl chloride (3-chloropropene)	45	400 at 27.5°C
557-40-4	Allyl ether	94	20[c]
557-31-3	Allyl ethyl ether	66	150[c]
870-23-5	Allyl mercaptan	67	100 at 15°C
627-40-7	Allyl methyl ether	55	300[c] at 25°C
1471-03-0	Allyl propyl ether	91	25[c]
100-52-7	Benzaldehyde[b]	178	1 at 26°C
109-65-9	1-Bromobutane	101.6	40 at 25°C
29576-14-5	1-Bromo-2-butene	98	70[c]
74-97-5	Bromochloromethane	68	100[c]
762-49-2	1-Bromo-2-fluoroethane	72	110[c]
107-82-4	1-Bromo-3-methylbutane	120.5	12 at 15°C
106-94-5	1-Bromopropane	71	100 at 18°C
75-26-3	2-Bromopropane	60	175[c]
75-62-7	Bromotrichloromethane	105	50[c]
109-79-5	*n*-Butylmercaptan	98	3.1
123-86-4	Butyl acetate	125	15[c]

(*Continued*)

CAS No.	Compound	Boiling Point (°C)	Vapor Pressure at 20°C (Torr)
71-36-3	*n*-Butyl alcohol[a]	117.2	4.4
78-92-2	*sec*-Butyl alcohol[a]	99.5	12
75-65-0	*tert*-Butyl alcohol[a]	83	31
109-69-3	*n*-Butyl chloride	78.4	80
78-86-4	*sec*-Butyl chloride	68	100 at 14°C
507-20-0	*tert*-Butyl chloride	51	375[c] at 30°C
628-81-9	Butyl ethyl ether	91.5	25[c]
123-72-8	Butyraldehyde[a]	75.7	71
141-75-3	Butyryl chloride	102	40[c]
142-96-1	*n*-Butyl ether[b]	141	4.8
75-87-6	Chloral (trichloroacetaldehyde)	97.8	39
107-20-0	Chloroacetaldehyde	90	50[c]
78-95-5	Chloroacetone[a]	119	25[c]
107-14-2	Chloroacetonitrile	127	79-04-9
79-04-9	Chloroacetyl chloride	107	35[c]
78-86-4	2-Chlorobutane	68.2	85[c]
928-51-8	4-Chloro-1-butanol	84.5	60[c]
4091-39-8	3-Chloro-2-butanone	116	30[c]
563-52-0	3-Chloro-1-butene	64	200[c]
1120-57-6	Chlorocyclobutane	83	140[c]
542-18-7	Chlorocyclohexane	143	10[c]
930-28-9	Chlorocyclopentane	114	60[c]
544-10-5	1-Chlorohexane[b]	134.5	20[c]
543-59-9	1-Chloropentane	108	75[c]
75-29-6	2-Chloropropane	35	450[c]
540-54-5	1-Chloropropane	46.6	375[c]
590-21-6	1-Chloropropene	37	400 at 18°C
557-98-2	2-Chloropropene	22.5	>700
95-49-8	2-Chlorotoluene[b] (α-tolylchloride)	159	5[c]
123-73-9	Crotonaldehyde[a] (2-butenal)	104	19
108-93-0	Cyclohexanol[b]	161	1
78-75-1	1,2-Dibromopropane[b]	141.5	7
109-64-8	1,3-Dibromopropane[b]	167	3[c]
594-16-1	2,2-Dibromopropane[b]	120	10[c]
79-02-7	Dichloroacetaldehyde	90.5	45[c]
513-88-2	1,1-Dichloroacetone	120	20[c]
616-21-7	1,2-Dichlorobutane	123.5	22[c]
541-33-3	1,1-Dichlorobutane	115	16[c]
7581-97-7	2,3-Dichlorobutane	116	17[c]
1190-22-3	1,3-Dichlorobutane[b]	134	10[c]
79-36-7	Dichloroacetyl chloride	109	15[c]
594-37-6	1,2-Dichloro-2-methylpropane	108	15[c]
78-99-9	1,1-Dichloropropane	88	45[c]
78-87-5	1,2-Dichloropropane	97	41
142-28-9	1,3-Dichloropropane	120.4	40[c]
594-20-7	2,2-Dichloropropane	69.3	60[c]
542-75-6	1.3-Dichloro-1-propene	108	39[c]
78-88-6	2,3-Dichloro-1-propene	84	53 at 25°C

(*Continued*)

CAS No.	Compound	Boiling Point (°C)	Vapor Pressure at 20°C (Torr)
60-29-7	Diethyl ether[a]	34.5	442
352-93-2	Diethyl sulfide	92	50[c]
108-20-3	Diisopropyl ether	69	130
75-18-3	Dimethyl sulfide	38	420
141-78-6	Ethyl acetate[a]	77	71
140-88-5	Ethyl acrylate[a]	100	29
97-95-0	2-Ethyl-1-butanol[b]	150	1.8
105-54-4	Ethyl butyrate	121	11.3
107-07-3	Ethylene chlorohydrin	128	4.9
109-94-4	Ethyl formate[a]	54	192
75-08-1	Ethyl mercaptan	36	440
97-63-2	Ethyl methacrylate	117	15[c]
110-43-0	2-Heptanone[b]	150	2.6
106-35-4	3-Heptanone[b]	148.5	1.4 at 25°C
123-19-3	4-Heptanone[b]	144	1.2 at 25°C
78-84-2	Isobutyraldehyde[a]	61.5	170
98-82-8	Isopropylbenzene[b] (cumene)	152.5	3.2
75-29-6	Isopropyl chloride	35.7	450[c]
108-21-4	Isopropyl acetate[a]	90	47.5
108-83-8	Isovalerone[b] (diisobutylketone)	165	1.7
513-36-0	Isobutyl chloride	69	100 at 16°C
590-86-3	Isovaleraldehyde	90	70[c]
126-98-7	Methacrylonitrile[a]	90.3	65 at 25°C
100-66-3	Methoxybenzene[b] (anisole)	155	5[c]
96-33-3	Methyl acrylate[a]	80	70
96-34-4	Methyl chloroacetate	130	10[c]
74-95-3	Methylene bromide	98	36
78-93-3	Methyl ethyl ketone[a]	79.6	77.5
74-88-4	Methyl iodide	42.5	400 at 25°C
563-80-4	Methyl isopropyl ketone	97.5	42 at 25°C
108-10-1	Methyl isobutyl ketone[a]	119	6
80-62-6	Methyl methacrylate	101	38[c] at 25°C
557-17-5	Methyl propyl ether	38.5	400 at 22.5°C
107-87-9	2-Pentanone[a]	101	13[c]
96-22-0	3-Pentanone[a]	102	13
109-60-4	*n*-Propyl acetate[a]	102	25
103-65-1	*n*-Propylbenzene[b]	159	2.5
107-19-7	Propargyl alcohol	115	
123-38-6	Propionaldehyde[a]	49	235
107-12-0	Propionitrile	97	40 at 22°C
107-03-9	*n*-Propyl mercaptan	68	150[c]
79-03-8	Propionyl chloride	80	85[c]
918-00-3	1,1,1-Trichloroacetone[b]	149	5[c]
76-02-8	Trichloroacetyl chloride	118	10[c]
10403-60-8	2,2,3-Trichlorobutane[b]	144	5[c]
96-18-4	1,2,3-Trichloropropane[b]	156	2
2567-14-8	1,1,2-Trichloropropylene	118	20[c]
354-58-5	1,1,1-Trichloro-2,2,2-trifluoroethane	46	275[c]

(*Continued*)

CAS No.	Compound	Boiling Point (°C)	Vapor Pressure at 20°C (Torr)
76-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane	48	270
110-62-3	Valeraldehyde	103	50 at 25°C
108-05-4	Vinyl acetate[a]	72	83
593-60-2	Vinyl bromide	15.8	>700
109-93-3	Vinyl ether	28	>600[c]

[a] Poor purging efficiency because of moderate solubility in water.
[b] Compounds show high retention times on the GC chromatogram.
[c] Vapor pressure estimated.

Appendix F: NIOSH Methods for Air Analysis

CAS No.	Analyte	NIOSH Method
[75-07-0]	Acetaldehyde	2538, 3500, 3507
[64-19-7]	Acetic acid	1603, 3501
[108-24-5]	Acetic anhydride	3506
[75-86-5]	Acetone cyanohydrin	2506
[75-05-8]	Acetonitrile	1606
–	Acids, inorganic	7903
[10035-10-6]	Hydrobromic acid	7903
[7664-38-2]	Hydrofluoric acid	7903
[7664-38-2]	Phosphoric acid	7903
[7647-01-0]	Hydrochloric acid	7903
[7697-37-2]	Nitric acid	7903
[7664-93-9]	Sulfuric acid	7903
[107-02-8]	Acrolein	2501
[107-13-1]	Acrylonitrile	1604, 2505
–	Alcohols	1400, 1401, 1402
[107-18-6]	Allyl alcohol	1402
[71-36-3]	*n*-Butyl alcohol	1401
[78-92-2]	*sec*-Butyl alcohol	1401
[75-65-0]	*tert*-Butyl alcohol	1400
[108-93-0]	Cyclohexanol	1402
[123-42-2]	Diacetone alcohol	1402
[64-17-5]	Ethanol	1400
[123-51-3]	Isoamyl alcohol	1402
[78-83-1]	Isobutyl alcohol	1401
[67-63-0]	Isopropyl alcohol	1400
[105-30-6]	Methyl isobutyl carbinol	1402
[71-23-8]	*n*-Propyl alcohol	1401
–	Aldehydes, screening	2539, 2531
–	Alkaline dusts	7401
[107-05-1]	Allyl chloride	1000
[7429-90-5]	Aluminum	7013
–	Amines, aliphatic	2010, 6010
[109-89-7]	Diethylamine	2010, 6010
[124-40-3]	Dimethylamine	2010, 6010
–	Amines, aromatic	2002
[62-53-3]	Aniline	2002
[121-69-7]	*N*,*N*-Dimethylaniline	2002
[99-97-8]	*N*,*N*-Dimethyl-*p*-toluidine	2002
[95-68-1]	α-Toluidine	2002
[95-68-1]	2,4-Xylidine	2002

(*Continued*)

CAS No.	Analyte	NIOSH Method
–	Aminoethanols	2007/3509
[141-43-5]	2-Aminoethanol (monoethanolamine)	2007/3509
[102-81-8]	2-(Dibutyl)aminoethanol	2007
[111-42-2]	Diethanolamine	3509, 5521
[100-37-8]	2-Diethylaminoethanol	2007
[102-71-6]	Triethanolamine	3509, 5521
[7664-41-7]	Ammonia	6701
[29191-52-4]	Anisidine	2514
[90-04-0]	*o*-Anisidine	2514
[104-94-9]	*p*-Anisidine	2514
[7440-38-2]	Arsenic	7900
–	Arsenic, organo	5022
[98-50-0]	*p*-Aminophenylarsonic acid	5022
–	Dimethylarsonic acid	5022
[124-58-3]	Methylarsonic acid	5022
[1237-53-3]	Arsenic trioxide	7901
[7784-42-1]	Arsine	6001
–	Asbestos, bulk	9002, 1300
–	Asbestos, fibers	7402, 6009
[123-99-9]	Azelaic acid	5019
–	Barium, soluble compounds	7056
[92-87-5]	Benzidine	5509
[94-36-0]	Benzoyl peroxide	5009
[7440-41-7]	Beryllium	7102
[92-52-4]	Biphenyl	2530
[12069-32-8]	Boron carbide	7506
[75-63-8]	Bromotrifluoromethane	1017
[1689-84-5]	Bromoxynil	5010
[1689-99-2]	Bromoxynil octanoate	5010
[106-99-0]	1,3-Butadiene	1024
[109-79-5]	1-Butanethiol	2525, 2537
[78-93-3]	2-Butanone	2500
[7440-43-9]	Cadmium	7048
[7440-70-2]	Calcium	7020
[63-25-2]	Carbaryl	5006
[1333-86-4]	Carbon black	5000
[75-15-0]	Carbon disulfide	1600
[55720-99-5]	Chlorinated diphenyl ether	5025
–	Chlorinated terphenyl	5014
[79-11-8]	Chloroacetic acid	2008
[126-99-8]	Chloroprene	1002
[7440-47-3]	Chromium	7024
–	Chromium, hexavalent	7600, 7604
[65996-93-2]	Coal tar pitch volatiles	5023
[7440-48-4]	Cobalt	7027
[7440-50-8]	Copper (dust and fumes)	7029
[1319-77-3]	Cresol	2001
–	Cyanides (aerosol and gas)	7904
[108-80-5]	Cyanuric acid	5030

(*Continued*)

CAS No.	Analyte	NIOSH Method
[542-92-7]	1,3-Cyclopentadiene	2523
[8065-48-3]	Demeton	5514
[334-88-3]	Diazomethane	2515
[19287-45-7]	Diborane	6006
[75-61-6]	Dibromodifluoromethane	1012
[107-66-4]	Dibutyl phosphate	5017
[91-94-1]	3,3′-Dichlorobenzidine	5509
[75-71-8]	Dichlorodifluoromethane	1018
[111-44-4]	*Sym*-dichloroethyl ether	1004
[75-43-4]	Dichlorofluoromethane	2516
[594-72-9]	1,1-Dichloro-1-nitroethane	1601
[76-14-2]	1,2-Dichlorotetrafluoroethane	1018
[127-19-5]	Dimethylacetamide	2004
[68-12-2]	Dimethylformamide	2004
[77-78-1]	Dimethyl sulfate	2524
[123-91-1]	Dioxane	1602
–	Dyes	5013
[90-04-0]	*o*-Anisidine	5013, 2514
[92-87-5]	Benzidine	5013, 2514
[119-93-7]	α-Tolidine	5013, 2514
[106-89-8]	Epichlorohydrin	1010
[2104-64-5]	EPN	5012
–	Esters	1450
[628-63-7]	*n*-Amyl acetate	1450
[626-38-0]	*sec*-Amyl acetate	1450
[123-86-4]	*n*-Butyl acetate	1450
[105-46-4]	*sec*-Butyl acetate	1450
[540-88-5]	*tert*-Butyl acetate	1450
[111-15-9]	2-Ethoxyethyl acetate	1450
[140-88-5]	Ethyl acrylate	1450
[123-92-2]	Isoamyl acetate	1450
[110-19-0]	Isobutyl acetate	1450
[108-84-9]	Methyl isoamyl acetate	1450
[109-60-4]	*n*-Propyl acetate	1450
–	Ethylene amines	2540
[111-40-0]	Diethylenetriamine	2540
[107-15-3]	Ethylenediamine	2540
[280-57-9]	Triethylenetetramine	2540
[107-07-3]	Ethylene chlorohydrin	2513
[107-21-1]	Etylene glycol	5500
[75-21-8]	Ethylene oxide	1614, 3702
[96-45-7]	Ethylene thiourea	5011
[60-29-7]	Ethyl ether	1610
–	Fibers	7400
[50-00-0]	Formaldehyde	2541, 3500, 3501
[98-01-1]	Furfural	2529
[98-00-0]	Furfuryl alcohol	2505
[111-30-8]	Glutaraldehyde	2531
[556-52-5]	Glycidol	1608
–	Glycol ethers	1403

(*Continued*)

CAS No.	Analyte	NIOSH Method
[111-76-2]	2-Butoxyethanol	1403
[110-80-5]	2-Ethoxyethanol	1403
[109-86-4]	2-Methoxyethanol	1403
[118-74-1]	Hexachlorobenzene	–
–	Hydrocarbons, alphatic and naphthenic	1500
[110-82-7]	Cyclohexane	1500
[110-83-8]	Cyclohexene	1500
[142-82-5	*n*-Heptane	1500
[110-54-3]	*n*-Hexane	1500
[111-65-9]	*n*-Pentane	1500
–	Hydrocarbons, aromatic	1501
[71-43-2]	Benzene	1501, 3700
[98-82-8]	*p-tert*-Butyltoluene	1501
[98-82-8]	Cumene	1501
[100-41-4]	Ethylbenzene	1501
[98-83-9]	α-Methylstyrene	1501
[91-20-3]	Napththalene	1501, 5506, 5515
[100-42-5]	Styrene	1501
[108-88-3]	Toluene	1501, 4000, 1501
[25013-15-4]	Vinyltoluene	1501
[1330-20-7]	Xylene	1501
–	Hydrocarbons, halogenated	1003
[100-44-7]	Benzyl chloride	1003
[75-25-2]	Bromoform	1003
[56-23-5]	Carbon tetrachloride	1003
[108-90-7]	Chlorobenzene	1003
[74-97-5]	Chlorobromomethane	1003
[67-66-3]	Chloroform	1003
[95-50-1]	*o*-Dichlorobenzene	1003
[106-46-7]	*p*-Dichlorobenzene	1003
[95-50-1]	1,2-Dichlorobenzene	1003
[549-59-0]	1,2-Dichloroethylene	1003
[107-06-2]	Ethylene dichloride	1003
[67-72-1]	Hexachloroethane	1003
[71-55-6]	Methylchloroform	1003
[127-18-4]	Tetrachloroethylene	1003
[79-00-5]	1,1,2-Trichloroethane	1003
[96-18-4]	1,2,3-Trichloropropane	1003
–	Hydrocarbons, halogenated (miscellaneous)	–
[107-05-1]	Allyl chloride	1000
[75-63-8]	Bromotrifluoromethane	1017
[75-61-6]	Dibromodifluoromethane	6006
[78-87-5]	1,2-Dichloropropane	1013
[74-96-4]	Ethyl bromide	1011
[75-00-3]	Ethyl chloride	2519
[106-93-4]	Ethylene dibromide	1008
[74-83-9]	Methyl bromide	2520
[74-87-3]	Methyl chloride	1001

(*Continued*)

CAS No.	Analyte	NIOSH Method
[75-09-2]	Methylene chloride	1005
[74-88-4]	Methyl iodide	1014
[76-01-7]	Pentachloroethane	2517
[79-27-6]	1,1,2,2-Tetrabromoethane	2003
[79-34-5]	1,1,2,2-Tetrachloroethane	1019
[79-01-5]	Trichloroethylene	1022, 3701
[593-60-2]	Vinyl bromide	1009
[75-01-4]	Vinyl chloride	1007
[75-35-4]	Vinylidene chloride	1015
[74-90-8]	Hydrogen cyanide	6010
[123-31-9]	Hydroquinone (1,4-benzenediol)	5004
[7553-56-2]	Iodine	6005
–	Isocyanate	5521
[584-84-9]	Toluene-2,4-diisocyanate	5521, 2535
[101-68-8]	4,4′-Methylenediphenyl isocyanate	5521
[822-06-0]	Hexamethylene diisocyanate	5521
[78-59-1]	Isophorone	2508
[143-50-0]	Kepone	5508
–	Ketones	–
[67-64-1]	Acetone	1300
[76-22-2]	Camphor	1301
[108-94-1]	Cyclohexanone	1300
[108-83-8]	Diisobutylketone	1300
[106-68-3]	Ethyl amyl ketone	1301
[106-35-4]	Ethyl butyl ketone	1301
[591-78-6]	2-Hexanone	1300
[141-79-7]	Mesityl oxide	1301
[583-60-8]	2-Methyl isobutyl ketone	1300
[110-43-0]	Methyl-*n*-amyl ketone	1301
[107-87-9]	2-Pentanone	1300
[7439-92-1]	Lead	7082
[1314-87-0]	Lead sulfide	7505
[121-75-5]	Malathion	5012
[7439-97-6]	Mercury	6009
[67-56-1]	Methanol	2000
[109-87-5]	Methylal	1611
[1338-23-4]	Methyl ethyl ketone peroxide	3508
[80-62-6]	Methyl methacrylate	2537
[7786-34-7]	Mevinphos	2503
[8012-95-1]	Mineral oil mist	5026
–	Naphthas	1550
–	Coal tar naphtha	1550
[8008-20-6]	Kerosene	1550
–	Mineral spirits	1550
[8032-32-4]	Petroleum ether	1550
[8030-30-6]	Petroleum naphtha	1550
–	Rubber solvent	1550
[8052-41-3]	Stoddart solvent	1550
–	Naphthylamines	5518

(*Continued*)

CAS No.	Analyte	NIOSH Method
[134-32-7]	α-Naphthylamine	5518
[91-59-8]	β-Naphthylamine	5518
[13463-39-3]	Nickel carbonyl	6007
–	Nitrobenzenes	2005
[100-00-5]	4-Chloronitrobenzene	2005
[98-95-3]	Nitrobenzene	2005
[88-72-2]	2-Nitrotoluene	2005
[99-08-1]	3-Nitrotoluene	2005
[99-99-0]	4-Nitrotoluene	2005
[79-24-3]	Nitroethane	2527
[10102-44-0]	Nitrogen dioxide	6700
[55-63-0]	Nitroglycerine	2507
[75-52-5]	Nitromethane	2527
[79-46-9]	2-Nitropropane	2528
–	Nitrosamines	2522
[924-16-3]	*N*-Nitrosodibutylamine	2522
[55-18-5]	*N*-Nitrosodiethylamine	2522
[62-75-9]	*N*-Nitrosodimethylamine	2522
[621-64-7]	*N*-Nitrosodipropylamine	2522
[59-89-2]	*N*-Nitrosomorpholine	2522
[100-75-4]	*N*-Nitrosopiperidine	2522
[930-55-2]	*N*-Nitrosopyrrolidine	2522
[10024-97-2]	Nitrous oxide	6600
–	Nuisance dust	–
–	Respirable	0600
–	Total	0500
[111-88-6]	1-Octanethiol	2510
–	Organotin compounds	5504
[7782-44-7]	Oxygen	6601
[4685-14-7]	Paraquat, tetrahydrate	5003
[56-38-2]	Parathion	5012
–	Pesticides and herbicides, chlorinated	–
[309-00-2]	Aldrin	5502
[57-74-9]	Chlordane	5510
[94-75-7]	2,4-D	5001
[72-20-8]	Endrin	5519
[58-89-9]	Lindane	5502
[93-76-5]	2,4,5-T	5001
[608-93-5]	Pentachlorobenzene	5517
[87-86-5]	Pentachlorophenol	5512
[108-95-2]	Phenol	3502
[7723-14-0]	Phosphorus	7905
[7719-12-2]	Phosphorus trichloride	6402
–	Polychlorinated biphenyls	5503
–	Polynuclear aromatic hydrocarbons	5506 (GC) or 5515 (HPLC)
[83-32-9]	Acenaphthene	5506 (GC) or 5515 (HPLC)

(*Continued*)

CAS No.	Analyte	NIOSH Method
[208-96-8]	Acenaphthylene	5506 (GC) or 5515 (HPLC)
[120-12-7]	Anthracene	5506 (GC) or 5515 (HPLC)
[56-55-3]	Benz[*a*]anthracene	5506 (GC) or 5515 (HPLC)
[205-99-2]	Benzo[*b*]fluoranthene	5506 (GC) or 5515 (HPLC)
[207-08-9]	Benzo[*k*]fluoranthene	5506 (GC) or 5515 (HPLC)
[191-24-2]	Benzo[*g,h,i*]perylene	5506 (GC) or 5515 (HPLC)
[192-97-2]	Benzo[*e*]pyrene	5506 (GC) or 5515 (HPLC)
[218-01-9]	Chrysene	5506 (GC) or 5515 (HPLC)
[53-70-3]	Dibenz[*a,h*]anthracene	5506 (GC) or 5515 (HPLC)
[206-44-0]	Fluoranthene	5506 (GC) or 5515 (HPLC)
[86-73-7]	Fluorene	5506 (GC) or 5515 (HPLC)
[193-39-5]	Indeno[1,2,3-*cd*]pyrene	5506 (GC) or 5515 (HPLC)
[91-20-3]	Naphthalene	5506 (GC) or 5515 (HPLC)
[85-01-8]	Phenanthrene	5506 (GC) or 5515 (HPLC)
[129-00-0]	Pyrene	5506 (GC) or 5515 (HPLC)
[75-56-9]	Propylene oxide	1612
[8003-34-7]	Pyrethrum	5008
[110-86-1]	Pyridine	1613
[14808-60-7]	Quartz (in coal mine dust)	7609
–	Ribaviron	5027
[83-79-4]	Rotenone	5007
–	Silica	–
–	Amorphous	7501
–	Crystalline (XRD)	7500
–	Crystalline (color)	7601
–	Crystalline (IR)	7602
[7803-52-3]	Stibine	6008
[57-24-9]	Strychnine	5016
[7446-09-5]	Sulfur dioxide	6004
[84-15-1]	α-Terphenyl	5021
[634-66-2]	1,2,3,4-Tetrachlorobenzene	–
[78-00-2]	Tetraethyl lead	2533
[107-49-3]	Tetraethyl pyrophosphate	2504
[109-99-9]	Tetrahydrofuran	1609
[75-74-1]	Tetramethyl lead	2534
[2782-91-4]	Tetramethyl thiourea	3505

(*Continued*)

CAS No.	Analyte	NIOSH Method
[137-26-8]	Thiram	5005
[95-80-7]	2,4-Toluenediamine	5516
[823-40-5]	2,6-Toluenediamine	5516
[584-84-9]	Toluene-2,4-diisocyanate	2535
[120-82-1]	1,2,4-Trichlorobenzene	5517
[129-79-3]	2,4,7-Trinitrofluoren-9-one	7074
[7440-33-7]	Tungsten	7074
[8006-64-2]	Turpentine	1551
[110-62-3]	Valeraldehyde	2536
–	Vanadium oxides	7504
[81-81-2]	Warfarin	5002
–	Welding and brazing fumes (metals)	7200
[7440-66-6]	Zinc	7030
[1314-13-2]	Zinc oxide	7502

Appendix G: U.S. EPA Methods for Air Analysis

There are 14 analytical methods developed by the U.S. EPA for measuring common organic pollutants in air. These analytes include aldehydes and ketones, chlorinated pesticides, polynuclear aromatic hydrocarbons, and many volatile organic compounds. These methods may also be applied to analyze other similar substances. All these methods are numbered from TO-1 to TO-14 and based on GC, GC/MS, and HPLC analytical techniques. Method numbers, sampling and analytical techniques, and the types of pollutants are outlined in Table G.1, while individual substances are listed in Table G.2.

TABLE G.1
Description of U.S. EPA Methods for Air Analysis

Method No.	Sampling and Analytical Techniques	Types of Pollutants
TO-1	Tenax adsorption, GC/MS analysis	Volatile, nonpolar organics in the BP range 80°C–200°C
TO-2	Carbon molecular sieve adsorption, GC/MS analysis	Highly volatile, nonpolar organics in the BP range −5°C to +120°C
TO-3	Cryogenic trapping, GC-FID, or ECD analysis	Volatile, nonpolar organics, in the BP range −10°C to +200°C
TO-4	High volume polyurethane foam sampling, GC/ECD analysis	Chlorinated pesticides and PCBs
TO-5	Derivatization with dinitrophenylhydrazine in impinger solution, HPLC-UV analysis	Aldehydes and ketones
TO-6	Bubbled through aniline solution; carbanilide formed; analyzed by HPLC	Phosgene
TO-7	Thermosorb/N adsorption; desorbed into methylene chloride; GC/MS analysis	*N*-Nitrosodimethylamine
TO-8	Sodium hydroxide impinger solution, HPLC analysis	Cresol and phenol
TO-9	High-volume polyurethane foam sampling with high resolution GC/high resolution MS (HRGC/HRMS) analysis	Polychlorinated dibenzo-*p*-dioxin
TO-10	Low-volume polyurethane foam sampling, GC-ECD analysis	Chlorinated pesticides
TO-11	DNPH-coated adsorbent cartridge; elution with acetonitrile; HPLC analysis	Formaldehyde
TO-12	Cryogenic preconcentration and direct flame ionization detection	Nonmethane type organic compounds
TO-13	Polyurethane foam/XAD-2 adsorption; GC and HPLC detection	Polynuclear aromatic hydrocarbons
TO-14	SUMMA passivated canister sampling; GC analysis using FID, ECD, NPD, PID, or GC/MS	Different types of organics including chlorinated and aromatic compounds

TABLE G.2
Individual Organic Pollutants in Air: U.S. EPA Methods

CAS No.	Aldehydes and Ketones	Method(s)
[75-07-0]	Acetaldehyde	TO-5, TO-11
[67-64-1]	Acetone	TO-5,TO-11
[107-02-8]	Acrolein	TO-5, TO-11
[100-52-7]	Benzaldehyde	TO-5, TO-11
[123-72-8]	Butyraldehyde	TO-5, TO-11
[123-73-9]	Crotonaldehyde	TO-5, TO-11
[5779-94-2]	2,5-Dimethylbenzaldehyde	TO-11
[50-00-0]	Formaldehyde	TO-5, TO-11
[66-25-1]	Hexanal	TO-5, TO-11
[78-84-2]	Isobutyraldehyde	TO-5
[590-86-3]	Isovaleraldehyde	TO-5, TO-11
[78-93-3]	Methyl ethyl ketone	TO-5
[110-62-3]	Pentanal	TO-5, TO-11
[123-38-6]	Propanal	TO-5, TO-11
[620-23-5]	*m*-Tolualdehyde	TO-5, TO-11
[529-20-4]	*o*-Tolualdehyde	TO-5, TO-11
[104-87-0]	*p*-Tolualdehyde	TO-5, TO-11
[110-62-3]	Valeraldehyde	TO-5, TO-11
[95-48-7]	*o*-Cresol	TO-8
[108-39-4]	*m*-Cresol	TO-8
[106-44-5]	*p*-Cresol	TO-8
	Miscellaneous Pollutants	
[75-69-4]	Freon-11	TO-14
[75-71-8]	Freon-12	TO-14
[76-13-1]	Freon-113	TO-14
[76-14-2]	Freon-114	TO-14
[118-74-1]	Hexachlorobenzene	TO-10
[87-68-3]	Hexachlorobutadiene	TO-14
[319-84-6]	α-Hexachlorocyclohexane	TO-10
[77-47-4]	Hexachlorocyclopentadiene	TO-10
[98-95-3]	Nitrobenzene	TO-1, TO-3
[62-75-9]	*N*-Nitrosodimethylamine	TO-7
[108-95-2]	Phenol	TO-8
[75-44-5]	Phosgene	TO-6
	Pesticides, Chlorinated	
[309-00-2]	Aldrin	TO-4, TO-10
[133-06-2]	Captan	TO-10
[57-74-9]	Chlordane	TO-4
[1897-45-6]	Chlorothalonil	TO-10
[2921-88-2]	Chlorpyrifos	TO-10
[72-55-9]	4,4′-DDE	TO-4, TO-10
[50-29-3]	4,4′-DDT	TO-4, TO-10
[62-73-7]	Dichlorovos	TO-10
[115-32-2]	Dicofol	TO-10
[60-57-1]	Dieldrin	TO-10
[72-20-8]	Endrin	TO-10

(*Continued*)

TABLE G.2 (*Continued*)
Individual Organic Pollutants in Air: U.S. EPA Methods

CAS No.	Aldehydes and Ketones	Method(s)
[7421-93-4]	Endrin aldehyde	TO-10
[133-07-3]	Folpet	TO-10
[76-44-8]	Heptachlor	TO-10
[1024-57-3]	Heptachlor epoxide	TO-10
[58-89-9]	Lindane	TO-10
[72-43-5]	Methoxychlor	TO-10
[315-18-4]	Mexacarbate	TO-10
[2385-85-5]	Mirex	TO-10
[39765-80-5]	*trans*-Nonachlor	TO-10
–	Oxychlordane	TO-10
[299-84-3]	Ronnel	TO-10
[608-93-5]	Pentachlorobenzene	TO-10
[87-86-5]	Pentachlorophenol	TO-10
–	Polychlorinated biphenyls	TO-4, TO-9
–	Polychlorinated dibenzo-ρ-dioxins	TO-9
[57653-85-7]	1,2,3,4,7,8-H_xCDD	TO-9
[3268-87-9]	Octachlorodibenzo-ρ-dioxin	TO-9
—	1,2,3,4-TCDD	TO-9
[1746-01-6]	2,3,7,8-TCDD	TO-9
	Polynuclear Aromatic Hydrocarbons	
[83-32-9]	Acenaphthene	TO-13
[208-96-8]	Acenaphthylene	TO-13
[120-12-7]	Anthracene	TO-13
[56-55-3]	Benz[*a*]anthracene	TO-13
[50-32-8]	Benzo[*a*]pyrene	TO-13
[205-99-2]	Benzo[*b*]fluoranthene	TO-13
[191-24-2]	Benzo[*g,h,i*]perylene	TO-13
[207-08-9]	Benzo[*k*]fluoranthene	TO-13
[218-01-9]	Chrysene	TO-13
[53-70-3]	Dibenz[*a,h*]anthracene	TO-13
[206-44-0]	Fluoranthene	TO-13
[86-73-7]	Fluorene	TO-13
[193-39-5]	Indeno[1,2,3-*cd*]pyrene	TO-13
[91-20-3]	Napththalene	TO-13
[85-01-8]	Phenanthrene	TO-13
[129-00-0]	Pyrene	TO-13
Volatile organic compounds		TO-1, TO-2,TO-3, TO-14
[107-13-1]	Acrylonitrile	TO-2, TO-3
[107-05-1]	Allyl chloride	TO-2, TO-3
[71-43-2]	Benzene	TO-1, TO-2, TO-3, TO-4
[56-23-5]	Carbon tetrachloride	TO-1,TO-2, TO-3, TO-4
[108-90-7]	Chlorobenzene	TO-1,TO-2,TO-14
[67-66-3]	Chloroform	TO-1, TO-2, TO-3, TO-14
[126-99-8]	Chloroprene (2-chloro-1,3-butadiene)	TO-1, TO-3
[98-82-8]	Cumene	TO-1
[106-93-4]	1,2-Dibromoethane	TO-14
[95-50-1]	1,2-Dichlorobenzene	TO-14

(*Continued*)

TABLE G.2 (*Continued*)
Individual Organic Pollutants in Air: U.S. EPA Methods

CAS No.	Aldehydes and Ketones	Method(s)
[541-73-1]	1,3-Dichlorobenzene	TO-14
[106-46-7]	1,4-Dichlorobenzene	TO-1, TO-3, TO-14
[75-34-3]	1,1-Dichloroethane	TO-14
[549-59-0]	1,2-Dichloroethylene	TO-14
[78-87-5]	1,2-Dichloropropane	TO-14
[142-28-9]	1,3-Dichloropropane	TO-14
[100-41-4]	Ethyl benzene	TO-14
[75-00-3]	Ethyl chloride	TO-14
[106-93-4]	Ethylene dibromide	TO-1
[107-06-02]	Ethylene dichloride (1,2-dichloroethane)	TO-1.TO-2, TO-3, TO-14
[622-96-8]	4-Ethyltoluene	TO-14
[74-87-3]	Methyl chloride (chloromethane)	TO-14
[75-09-2]	Methylene chloride (dichloromethane)	TO-2, TO-3, TO-14
[79-34-5]	1,1,2,2-Tetrachloroethane	TO-14
[127-18-4]	Tetrachloroethylene	TO-14
[108-88-3]	Toluene	TO-1, TO-2, TO-3, TO-14
[75-25-2]	Tribromomethane (bromoform)	TO-1
[71-55-6]	1,1,1-Trichloroethane (methyl chloroform)	TO-1,TO-2, TO-3, TO-14
[79-00-5]	1,1,2-Trichloroethane	TO-14
[79-01-5]	Trichloroethylene	TO-1, TO-2, TO-3, TO-14
[100-42-5]	Vinyl benzene (styrene)	TO-14
[75-01-4]	Vinyl chloride	TO-2, TO-3, TO-14
[75-35-4]	Vinylidine chloride (1,1-dichloroethylene)	TO-2, TO-3, TO-14
[95-47-6]	*o*-Xylene	TO-1, TO-2, TO-14
[108-38-3]	*m*-Xylene	TO-1, TO-2, TO-14
[106-42-3]	*p*-Xylene	TO-1, TO-2, TO-14

Appendix H: Inorganic Test Procedures for Analysis of Aqueous Samples: EPA, SM, and ASTM Reference Methods

Analytes, Types of Analysis	U.S. EPA Methods	Standard Method (Vol. 18)	ASTM
Acidity, as mg $CaCO_3$/L			
Amperometric titrations	305.1	2310 B	D1067-88
Phenolphthalein titrations	305.1	2310 B	–
Alkalinity, as mg $CaCO_3$/L			
Electrometric or colorimetric	310.1	2310 B	D1067-88
Manual titration	310.1	2320 B	–
Automate	310.2	–	–
Aluminum			
AA direct aspiration	202.1	3500-A1 B	–
AA furnace	202.2	3500-A1 B	–
ICP	200.7	3500-A1 C	D4190-88
DCP	–	–	–
Colorimetric (eriochrome cyanine R)	–	3500-A1 D	–
Ammonia (as N)			
Colorimetric nesslerization	350.2	4500-NH_3 C	D1426-79(A)
Titration	350.2	4500-NH_3 E	–
Electrode	350.3	4500-NH_3 F	D1426-79(D)
Automated phenate	350.1	4500-NH_3 H	D1426-79(C)
Colorimetric phenate	–	4500-NH_3 D	–
Antimony			
AA direct aspiration	204.1	3500-Sb B	–
AA furnace	204.2	3500-Sb B	–
ICP	200.7	3500-Sb D	–
Arsenic			
AA gaseous hydride	206.3	3500-As B	D2972-84(B)
AA furnace	206.2	3500-As B	–
ICP	200.7	3500-As D	–
Colorimetric (SDDC)	206.4	3500-As C	D2972-84(A)
Barium			
AA direct aspiration	208.1	3500-Ba B	–
AA furnace	206.2	3500-Ba B	–
ICP	200.7	3500-Ba C	–

(*Continued*)

Analytes, Types of Analysis	U.S. EPA Methods	Standard Method (Vol. 18)	ASTM
Beryllium			
AA direct aspiration	210.1	3500-Be B	D3645-84-88(A)
AA furnace	210.2	3500-Be B	–
ICP	200.7	3500-Be C	–
DCP		3500-Be D	D4190-88
Colorimetric (aluminon)			—
Biochemical oxygen demand (dissolved oxygen depletion)	405.1	5210 B	–
Boron			
Colorimetric (curcumin)	212.3	4500-B B	–
TCP	200.7	4500-B D	–
DCP	200.7	4500-B D	D4190-88
Bromide			
Colorimetric, phenol red	–	4500-Br B	–
Ion chromatography	–	4110	–
Titrimetric	320.1	–	D1246-82C
Cadmium			
AA direct aspiration	213.1	3500-Cd B	D3557-90(A, B)
AA furnace	213.2	3500-Cd B	
ICP	200.7	3500-Cd C	
DCP			D4190-90
Colorimetric (dithiozone)		3500-Cd D	
Calcium			
AA direct aspiration	215.1	3500-Ca B	D511-88(B)
ICP	200.7	3500-Ca C	
Titrimetric (EDTA)	215.2	3500-Ca D	D511-88(A)
Chemical oxygen demand			
Titrimetric	410.1	5220 C	D1252-88
Colorimetric	410.4	5220 D	–
Chloride			
Titrimetric (silver nitrate)	–	4500-Cl B	D512-89(B)
Titrimetric (mercuric nitrate)	325.3	4500-Cl C	D512-89(A)
Colorimetric, manual	–	–	D512-89(c)
Automated (ferricyanide)	325.1 325.2	4500-Cl E	–
Potentiometric titration	–	4500-Cl D	–
Ion chromatography	–	4110	–
Chlorine, residual			
Amperometric titration	330.1	4500-Cl E	D1253-76(A)
Iodometric direct titration	330.3	4500-Cl B	D1253-76(B)
Iodometric back titration	330.2	4500-Cl C	–
PD-FAS titration	330.4	4500-Cl F	–
PD-colorimetric	330.5	4500-Cl G	–
Chromium VI (dissolved)			
A chelation extraction	218.4	3111 C	–
Colorimetric-diphenylcarbazide	–	3500-Cr D	–

(*Continued*)

Analytes, Types of Analysis	U.S. EPA Methods	Standard Method (Vol. 18)	ASTM
Chromium, total			
A direct aspiration	218.1	3500-Cr B	D1687-86(D)
A chelation extraction	218.3	3111 C	–
A furnace	218.2	3500-Cr B	–
CP	200.7	3500-Cr C	–
CP	–	–	D4190-88
Colorimetric-diphenylcarbazide	–	3500-Cr D	D1687-86(A)
Cobalt			
A direct aspiration	219.1	3500-Co B	D3558-90
A furnace	219.2	3500-Co B	–
CP	200.7	3500-Co C	–
DCP	–	–	D4190-88
Color			
Colorimetric (ADMI)	110.1	2120 E	
Platinum–cobalt	110.2	2120 B	
Spectrophotometric	110.3	2120 C	
Copper			
AA direct aspiration	220.1	3500-Cu B	D1688-90 (A, B)
AA furnace	220.2	3500-Cu B	
ICP	200.7	3500-Cu C	
DCP	–	–	D4190-88
Colorimetric (neo cuproine)	–	3500-Cu D	D1688-84(88)(A)
Cyanide, total			
Titrimetric	–	4500-CN D	–
Spectrophotometric	335.2	4500-CN D	D2036-89(A)
Automated	335.3	–	D2036-89(A)
Electrode	–	4500-CN F	–
Cynanide amenable to chlorination	335.1	4500-CN G, H	D2036-89(B)
Fluoride			
Electrode	340.2	4500-F C	D1179-88(B)
Colorimetric (SPADNS)	340.1	4500-F D	D1179-88(A)
Automated complexone	340.3	4500-F E	–
Ion chromatography	–	4110	–
Gold			
Direct aspiration	231.1	3500-Au B	
AA furnace	231.2	3500-Au B	
Hardness			
Automated colorimetric	130.1	3500-Ir B	–
EDTA titration or Ca and Mg by AA	130.2	3500-Ir B	D1126-86 (1990)
Iridium			
AA direct aspiration	235.1	3500-Ir B	–
AA furnace	232.2	3500-Ir B	–
Iron			
AA direct aspiration	236.1	3500-Fe B	D1068-90(A, B)
AA furnace	236.2	3500-Fe B	

(*Continued*)

Analytes, Types of Analysis	U.S. EPA Methods	Standard Method (Vol. 18)	ASTM
ICP	200.7	3500-Fe C	
Colorimetric (phenanthroline)	–	3500-Fe D	D1068-90(D)
Kjeldahl nitrogen	–	4500-N_{org}	3590-84(A)
Titration	351.3	B or C	D3590-89(A)
Nesslerization	351.3	–	D3590-89(A)
Electrode	351.3	–	–
Automated phenate	351.1	–	
Semiautomated block digester	351.2	–	D3590-89(B)
Potentiometric	351.4	–	D3590-89(A)
Lead			
AA direct aspiration	239.1	3500-Pb B	D3559-90(A, B)
AA furnace	239.2	3500-Pb B	–
ICP	200.7	3500-Pb C	–
DCP	–	–	D4190-88
Voltammetry	–	–	D3559-90(C)
Colorimetric (dithiozone)	–	3500-Pb D	–
Magnesium			
AA direct aspiration	242.1	3500-Mg B	D511-88(B)
ICP	200.7	3500-Mg C	
Gravimetric	–	3500-Mg D	D511-77(A)
Manganese			
AA direct aspiration	243.1	3500-Mn B	D858-90(A, B)
AA furnace	243.2	3500-Mn B	–
ICP	200.7	3500-Mn C	
DCP	–	–	D4190-88
Colorimetric, persulfate	–	3500-Mn D	D858-84(A) (1988)
Mercury			
Cold vapor, manual	245.1	3500-Hg B	D3223-86
Automated	245.2	–	–
Molybdenum			
AA direct aspiration	246.1	3500-Mo B	–
AA furnace	246.2	3500-Mo B	
ICP	200.7	3500-Mo C	
Nickel			
AA direct aspiration	249.1	3500-Ni B	D1886-90(A, B)
AA furnace	249.2	3500-Ni B	–
ICP	200.7	3500-Ni C	–
DCP	–	–	D4190-88
Nitrate (as N)			
Electrode method	–	4500-NO_3 C	–
Ion chromatography	–	4110	–
Colorimetric	352.1	–	D992-71
Nitrate–nitrite (as N)			
Cd reduction, manual or automated	353.3	4500-NO_3 E	D3867-90(B)
	353.2	4500-NO_3 F	D3867-90(A)
Hydrazine reduction (automated)	353.1	4500-NO_3 H	–

(*Continued*)

Analytes, Types of Analysis	U.S. EPA Methods	Standard Method (Vol. 18)	ASTM
Nitrite (as N)			
Colorimetric, manual	354.1	4500- NO_2^- B	D1254-67
Oil and grease			
Gravimetric	413.1	5520 B	–
Infrared method	–	5520 C	–
Orthophosphate (as P)			
Ascorbic acid method	–	4500-P E	–
Automated	365.1	–	
Manual, single reagent	365.2	–	D515.88(A)
Manual, two reagent	365.3	–	–
Vanadomolyldophosphoric acid	–	4500-P C	–
Osmium			
AA direct aspiration	252.1	3500-Os B	–
AA furnace	252.2	3500-Os B	–
Oxygen, dissolved			
Winkler (azide modification)	360.2	4500-O C	D888-81 (C) (1988)
Electrode	360.1	4500-O G	–
Ozone, residual			
Colorimetric, indigo	–	4500-O_3	–
pH electrometric	150	4500-H^+	D1293-84(AB) (1990)
Palladium			
AA direct aspiration	253.1	3500-Pd B	–
AA furnace	253.2	3500-Pd B	–
Phenols	–	5530	–
Colorimetric, manual	420.1	–	D1783-80(A, B)
Automated	420.2	–	–
Phosphorus, total	–	4500 P	–
Colorimetric, manual	365.2	–	D515-88(A)
Automated, ascorbic acid	365.1	–	–
Semiautomated	365.4	–	–
Platinum			
AA direct aspiration	255.1	3500-Pt B	–
AA furnace	255.2	3500-Pt B	–
Potassium			
AA direct aspiration	258.1	3500-K B	–
ICP	200.7	3500-K C	–
Flame photometric	–	3599-K D	D 1428-82(A)
Residue, total	160.3	2540 B	–
Filterable	160	2540 C	–
Nonfilterable (TSS)	160.2	2540 D	–
Settleable	160.5	2540 F	–
Volatile	160.4	2540 G	–
Rhodium			
AA direct aspiration	265.1	3500-Rh B	–
AA furnace	265.2	3500-Rh B	–

(*Continued*)

Analytes, Types of Analysis	U.S. EPA Methods	Standard Method (Vol. 18)	ASTM
Ruthenium			
AA direct aspiration	267.1	3500-Ru B	–
AA furnace	267.2	3500-Ru B	–
AA gaseous hydride	270.3	3500-Se C	D3859-88(A)
Silica, dissolved			
Colorimetric	370.1	–	D859-88(B)
Silver			
AA direct aspiration	272.1	3500-Ag B	–
AA furnace	272.2	3500-Ag B	–
ICP	200.7	3500-Ag C	–
Sodium			
AA direct aspiration	273.1	3500-Na B	–
ICP	200.7	3500-Na C	–
Flame photometric	–	3500-Na D	D1428-82(A)
Specific conductance			
Wheatstone bridge	120.1	2510	D1125-82(A)
Sulfate			
Gravimetric	375.3	4500-SO_4^{2-} C, D	D516-82A (1988)
Turbidimetric	375.4	4500-SO_4^{2-} E	D516-88
Colorimetric, automated (barium chloranilate)	375.1	4500-SO_4^{2-} F	–
Ion chromatography	–	4110	–
Sulfide			
Iodometric titration	376.1	4500-S^{2-} E	–
Colorimetric (methylene blue)	376.2	4500-S^{2-} D	–
Sulfite			
Titrimetric	377.1	4500-SO_3^{2-} B	D1339-84(C)
Surfactants			
Colorimetric (methylene blue)	425.1	5540 C	D2330-88
Temperature	170.1	2550	–
Thallium			
AA direct aspiration	279.1	3500-TL B	–
AA furnace	279.2	3500-TL B	–
ICP	200.7	3500-TL C	–
Tin			
AA direct aspiration	282.1	3500-Sn B	–
AA furnace	282.2	3500-Sn B	–
Titanium			
AA direct aspiration	283.1	3500-Ti B	–
AA furnace	283.2	3500-Ti B	–
Total organic carbon (TOC) combustion	415.1	–	D2579-85(A, B)

(*Continued*)

Analytes, Types of Analysis	U.S. EPA Methods	Standard Method (Vol. 18)	ASTM
Turbidity			
Nephelometric	180.1	–	D1889-88(A)
Vanadium			
AA direct aspiration	286.1	3500-V B	–
AA furnace	286.2	3500-V B	–
ICP	200.7	3500-V C	–
DCP	–	–	D4190-88
Colorimetric (gallic acid)	–	3500-V D	D3373-84(A) (1988)
Zinc			
AA direct aspiration	289.1	3500-Zn B	D1691.90(A, B)
AA furnace	289.2	3500-Zn B	–
ICP	200.7	3500-Zn C	–
DCP	–	–	D4190-88
Colorimetric			
Dithizon	–	3500-Zn D, E	–
Zincon	–	3500-Zn F	–

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Appendix I: U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices

The U.S. EPA's major analytical methods for the determination of organic pollutants in aqueous and solid matrices are presented in the following table. Organic compounds, their CAS registry numbers, the types or classes to which they belong, the EPA method numbers, and the instrumental techniques for analysis are listed in the table. This, however, is not a complete or updated list of all methods. Many methods are still in proposed status. In the table below, the sample extraction techniques are not mentioned. This is excluded because most of these compounds can be extracted by more than one specific method. Readers should refer to the specific EPA methods for the detailed procedures, including sample preparation, cleanup steps, chromatographic conditions, and the QA/QC requirements.

The analytical methods in the series 500 are addressed to potable waters, while the methods in the 600 series refer to the analyses of wastewater. Methods in the 8000 series refer to the instrumental analysis of organic pollutants in several types of matrices, including groundwater, soils, sediments, and hazardous wastes. Methods for sample extractions for the 8000 series are written separately under the 3000 series, which should go in conjunction with the 8000 series. The extraction methods under the 3000 series are not presented in this appendix. None of these three parallel series of methods under 500, 600, and 8000, differ significantly from each other. In addition, a few methods under 1600 are similar to the above methods. These methods are not included in the table.

The instrumentation techniques are primarily GC, GC/MS, and HPLC. The term GC-HSD refers to the halide-specific detector that includes the Hall electrolytic conductivity detector and the microcoulometric detector. For such analysis, either of these detectors may be used. An electron capture detector (ECD) may be effective to a lesser extent for GC-HSD measurement. NPD and FPD refer to nitrogen–phosphorus detector and flame photometric detector, respectively. GC-FID (flame ionization detector) and GC/MS (mass spectrometer) are the most versatile instrumental techniques. HPLC methods primarily require the use of either a fluorescence detector (HPLC-FL) or an UV detector (HPLC-UV).

U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
Acenaphthene	83-32-9	PAH	550.1	HPLC-UV
			610	HPLC-UV
			625	GC/MS
			8310	HPLC-UV
			8270	GC/MS
			OLMO1	GC/MS
Acenaphthylene	208-96-8	Polynuclear aromatic hydrocarbon	525	GC/MS
			550.1	HPLC-UV
			610	HPLC-UV
			625	GC/MS
			8310	HPLC-UV
			8270	GC/MS
			OLMO1	GC/MS
Acetamidofluorene	53-96-3	Polynuclearamide	8270	GC/MS
Acetone (2-propanone)	67-64-1	VOC (ketone)	OLMO1	GC/MS
Acetophenone (1-penylethanone)	98-86-2	Aromatic ketone	8270	GC/MS
1-Acetyl-2-thiourea	591-08-2	Thiourea	8270	GC/MS
Aciflurofen	50594-66-6	Pesticide, chlorinated	515.1	GC-ECD
Acrolein (2-propenal)	107-02-8	Aldehyde (VOC)	603	GC-FID
			624	GC/MS
Acrylonitrile (vinyl cyanide)	107-13-1	VOC (nitrate)	603	GC-FID
			624	GC/MS
Alachlor (Metachlor, Lasso)	15972-60-8	Pesticide, chlorinated	505	GC-ECD
			507	GC-NPD
			525	GC/MS
Aldicarb (Temik)	116-06-3	Pesticide, carbamate	531.1	HPLC-FL
Aldicarb sulfone (Aldoxycarb)	1646-88-4	Pesticide, carbamate	531.1	HPLC-FL
Aldicarb sulfoxide	1646-87-3	Pesticide, carbamate	531.1	HPLC-FL
Aldrin	309-00-2	Pesticide, organochlorine	505	GC-ECD
			508	GC-ECD
			525	GC/MS
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Allyl chloride (3-chlor-1-propene)	107-05-1	Halogenated hydrocarbon (VOC)		
2-Aminoanthraquinone	117-79-3	Aromatic ketone	8270	GC/MS
4-Aminobiphenyl	92-67-1	Aromaticamine	8270	GC/MS
Anilazine (dyrene)	101-05-3	Triazine	8270	GC/MS
Aniline (aminobenzene)	62-53-3	Aromaticamine	8270	GC/MS
o-Anisidine	90-04-0	Aromatic amine	8270	GC/MS
Anthracene	120-12-7	Polynuclear aromatic hydrocarbons	525	GC/MS
			550.1	HPLC-FL
			610	HPLC-FL
			625	GC/MS
			8310	HPLC-FL
			8270	GC/MS
			OLMO1	GC/MS

(*Continued*)

U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
Aramite	140-57-8	Pesticide, organosulfur	8270	GC/MS
Aroclor-1016 (PCB-1016)	12674-11-2	Polychlorinated biphenyl	505	GC-ECD
			508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Aroclor-1221 (PCB-1221)	11104-28-2	Polychlorinated biphenyl	505	GC-ECD
			508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Aroclor-1232 (PCB-1232)	11141-16-5	Polychlorinated biphenyl	505	GC-ECD
			508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Aroclor-1242 (PCB-1242)	53469-21-9	Polychlorinated biphenyl	505	GC-ECD
			508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Aroclor-1248 (PCB-1248)	12672-29-6	Polychlorinated biphenyl	505	GC-ECD
			508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Aroclor-1254	11097-69-1	Polychlorinated biphenyl	505	GC-ECD
			508	GC-ECD
			608	GC-ECD
			8080	GC-ECD
			625	GC/MS
			8270	GC/MS
			OLMO1	GC-ECD
Aroclor-1260 (PCB-1260)	11096-82-5	Polychlorinated biphenyl	505	GC-ECD
			508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD

(*Continued*)

U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
Atrazine	1912-24-9	Pesticide, triazine	505	GC-ECD
			507	GC-NPD
			525	GC/MS
Avadex	2303-16-4	Pesticide, carbamate	8270	GC/MS
Azinphos-methyl (Guthion)	86-50-0	Organophosphorus pesticide	8140	GC-FPD
			8270	GC/MS
Barban (Carbyn)	101-27-9	Pesticide, carbamate	8270	GC/MS
Basalin	33245-39-5	Pesticide, chlorinated	8270	GC/MS
Baygon (Propoxur)	114-26-1	Pesticide, carbamate	531.1	HPLC-FL
Benzal chloride (dichloromethyl benzene)	98-87-3	Halogenated hydrocarbon	8120	GC-ECD
Benzene	71-43-2	Aromatic	502.2	GC-PID
			524.2	GC/MS
			602	GC-PID
			624	GC/MS
			8260	GC/MS
			8020	GC-PID
			OLMO1	GC/MS
1,4-Benzenediamine (*p*-phenylenediamine)	106-50-3	Aromatic amine	8270	GC/MS
Benzidine	92-87-5	Aromatic amine	605	HPLC-EL
			625	GC/MS
			8270	GC/MS
Benzo[*a*]anthracene	56-55-3	PAH	550.1	HPLC-FL
			525	GC/MS
			610	HPLC-FL
			625	GC/MS
			8310	HPLC-FL
			8270	GC/MS
			OLMO1	GC/MS
Benzo[*b*]fluoranthene	205-99-2	Polynuclear aromatic hydrocarbon	550.1	HPLC-FL
			610	HPLC-FL
			625	GC/MS
			8310	HPLC-FL
			8270	GC/MS
			OLMO1	GC/MS
Benzo[*j*]fluoranthene	205-82-3	Polynuclear aromatic hydrocarbon	525	GC/MS
Benzo[*k*]fluoranthene	207-08-9	Polynuclear aromatic hydrocarbon	525	GC/MS
			550.1	HPLC-FL
			610	HPLC-FL
			625	GC/MS
			8310	HPLC-FL
			8270	GC/MS
			OLMO1	GC/MS
Benzo[*g,h,i*]perylene	191-24-2	Polynuclear aromatic hydrocarbon	525	GC/MS
			550.1	HPLC-FL
			610	HPLC-FL
			625	GC/MS
			8310	HPLC-FL
			8270	GC/MS
			OLMO1	GC/MS

(*Continued*)

U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
Benzo[*a*] pyrene	50-32-8	Polynuclear aromatic hydrocarbon	550.1	HPLC-FL
			525	GC/MS
			610	HPLC-FL
			625	GC/MS
			8310	HPLC-FL
			8270	GC/MS
			OLMO1	GC/MS
Benzoic acid (benzenecarboxylic acid)	65-85-0	Carboxylic acid	8270	GC/MS
Benzyl alcohol	100-51-6	Aromatic alcohol	8270	GC/MS
Benzyl chloride [(chloromethyl) benzene]	100-44-7	Chlorinated hydrocarbon	8120	GC-ECD
BHC (hexachlorocyclohexane)	608-73-1	Pesticide, chlorinated	8120	GC-ECD
α-BHC	319-84-6	Pesticide, chlorinated	508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
β-BHC	319-85-7	Pesticide, chlorinated	508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Δ-BHC	319-86-8	Pesticide, chlorinated	508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Bromacil	314-40-9	Pesticide, urea	507	GC-NPD
Bromobenzene	108-86-1	Halogenated hydrocarbon	502.2	GC-ELCD/PID
			524.2	GC/MS
			8260	GC/MS
Bromochloromethane (chlorobromomethane)	74-97-5	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			8260	GC/MS
Bromoform	75-25-2	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
4-Bromophenylphenylether (1-bromo-4-phenoxybenzene)	101-55-3	Haloether	611	GC-HSD
			625	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
Bromoxynil	1689-84-5	Bromonitrile	8270	GC/MS
n-Butyl benzene	104-51-8	VOC (aromatic)	502.2	GC-PID
			524.2	GC/MS
			8260	GC/MS

(*Continued*)

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Compounds	CAS No.	Type/Class	Method #	Techniques
sec-Butylbenzene	135-98-8	Aromatic	502.2	GC-PID
			524.2	GC/MS
			8260	GC/MS
tert-Butylbenzene	98-06-6	Aromatic	502.2	GC-ELCD
			524.2	GC/MS
			8260	GC/MS
Butyl benzyl phthalate	85-68-7	Phthalate ester	525	GC/MS
			606	GC-ECD
			625	GC/MS
			8060	GC-ECD/FID
			8270	GC/MS
			OLOM1	GC/MS
Captafol (Difolatan)	2425-06-1	Pesticide, thiocarboximide	8270	GC/MS
Captan (Ortholide-406)	133-06-2	Pesticide, carbamate	8270	GC/MS
Carbaryl	63-25-2	Pesticide, carbamate	531.1	HPLC-FL
			8270	GC/MS
Carbazole	86-74-8	Heteroclic nitrogen compound	OLMO1	GC/MS
Carbofuran (Furadan)	1563-66-2	Pesticide, carbamate	531.1	HPLC-FL
			8270	GC/MS
Carbon disulfide	75-15-0	Organic sulfide	OLMO1	GC/MS
Carbon tetrachloride	56-23-5	VOC (halogenated organic)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
CDEC (sulfallate)	95-06-7	Pesticide, thiocarbamate	8270	GC/MS
Chlordane	57-74-9	Pesticide, chlorinated	505	GC-ECD
			508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
α-Chlordane	5103-71-9	Pesticide, chlorinated	505	GC-ECD
			508	GC-ECD
			525	GC/MS
			608	GC-ECD
			625	GC/MS
			OLMO1	GC-ECD
γ-Chlordane	5103-74-2	Pesticide, organochlorine	505	GC-ECD
			508	GC-ECD
			525	GC/MS
			608	GC-ECD
			625	GC/MS
			OLMO1	GC-ECD
Chlorfenvinphos	470-90-6	Pesticide, organophosphorus	8270	GC/MS
4-Chloro-3-methylphenol	59-50-7	Phenol	604	GC-ECD/FID
			625	GC/MS
			8040	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS

(*Continued*)

U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
4-Chloroaniline	106-47-8	Halogenated amine	8270	GC/MS
			OLMO1	GC/MS
Chlorobenzene	108-90-7	Halogenated hydrocarbon	502.2	GC-ELCD/PID
			524.2	GC/MS
			601	GC-HSD
			602	GC-PID
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
Chlorobenzilate (Acaraben)	510-15-6	Pesticide, chlorinated	508	GC-ECD
			8270	GC/MS
Bis-(2-chloroethoxy) methane	111-91-1	Haloether	611	GC-HSD
			625	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
2-Chloroethylvinyl ether	110-75-8	Haloether	601	GC-HSD
			624	GC/MS
Chloroform	67-66-3	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
Bis-(2-chloroisopropyl) ether	108-60-1	Haloether	625	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
3-Chloromethylpyridine hydrochloride	6959-48-4	Pyridine, substituted	8270	GC/MS
1-Chloronaphthalene	90-13-1	Chlorinated hydrocarbon	8270	GC/MS
2-Chloronaphthalene	91-58-7	Chlorinated hydrocarbon	612	GC-ECD
			625	GC/MS
			8120	GC-ECD
			8270	GC/MS
			OLMO1	GC/MS
5-Chloro-*o*-toluidine	95-79-4	Aromatic amine	8270	GC/MS
2-Chlorophenol	95-57-8	Phenol	604	GC-FID/ECD
			625	GC/MS
			8040	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS
4-Chlorophenyl phenyl ether (1-chloro-4-phenoxybenzene)	7005-72-3	Haloether	625	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
Chlorothalonil (Daconil 2787)	1897-45-6	Pesticide, chlorinated	508	GC-ECD
o-Chlorotoluene	95-49-8	VOC (halocarbon)	502.2	GC-ELCD/PID
			524.2	GC/MS
			8260	GC/MS
p-Chlorotoluene	106-43-4	VOC (halogenated hydrocarbon)	502.2	GC-ELCD/PID
			524.2	GC/MS
			8260	GC/MS

(*Continued*)

U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
Chrysene	218-01-9	Polynuclear aromatic hydrocarbon	525	GC/MS
			550.1	HPLC-FL
			610	HPLC-UV
			625	GC/MS
			8310	HPLC-FL
			8270	GC/MS
			OLMO1	GC/MS
Coumaphos	56-72-4	Pesticide, organophosphorus	8140	GC-FPD
			8270	GC/MS
m-Cresol (3-methylphenol)	108-39-4	Phenol	8270	GC/MS
o-Cresol (2-methylphenol)	95-48-7	Phenol	8270	GC/MS
			OLMO1	GC/MS
p-Cresol (4-methylphenol)	106-44-5	Phenol	8270	GC/MS
			OLMO1	GC/MS
Cresylic acid	1319-77-3	Phenol	8040	GC-FID
Crotoxyphos	7700-17-6	Pesticide, organophosphorus	8270	GC/MS
Cumene (isopropylbenzene)	98-82-8	VOC (aromatic)	502.2	GC-PID
			524.2	GC/MS
			8260	GC/MS
p-Cymene (*p*-isopropyl toluene)	99-87-6	VOC (aromatic)	502.2	GC-PID
			524.2	GC/MS
			8260	GC/MS
2,4-D	94-75-7	Chlorophenoxy acid herbicide	515.1	GC-ECD
			8150	GC-ECD
Dacthal (DCPA)	1861-32-1	Chlorinated aromatic	508	GC-ECD
Dalapon (2,2-dichloropropanoic acid)	75-99-0	Pesticide, chlorinated	515.1	GC-ECD
			8150	GC-ECD
4,4′-DDD	72-54-8	Chlorinated pesticide	508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
4,4′-DDE	72-55-9	Chlorinated pesticide	508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
4,4′-DDT	50-29-03	Chlorinated pesticide	508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC-ECD
			OLMO1	GC/MS
o, *p*-DDT	789-02-6	Pesticide, chlorinated	625	GC/MS
Dechlorane	2385-85-5	Pesticide, chlorinated	8270	GC/MS
2,4-Diaminotoluene	95-80-7	Aromatic amine	8270	GC/MS
Diazinon (Basudin)	333-41-5	Pesticide, organophosphorus	507	GC-NPD
			8140	GC-FPD

(*Continued*)

U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
Dibenz[*a*,*j*]acridine	224-42-0	Polynuclear aromatic hydrocarbon	8270	GC/MS
Dibenz[*a*,*h*]anthracene	53-70-3	Polynuclear aromatic hydrocarbon	515.1	HPLC-FL
			525	GC/MS
			610	HPLC-FL
			625	GC/MS
			8310	HPLC-FL
			8270	GC/MS
			OLMO1	GC/MS
Dibenzofuran	132-64-9	Benzofuran	8270	GC/MS
			OLMO1	GC/MS
Dibenzo[*a*,*e*]pyrene	192.65.4	Polynuclear aromatic hydrocarbon	8270	GC/MS
Dibromochloromethane	124-48-1	Halogenated hydrocarbon (VOC)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
Dibromochloropropane	96-12-8	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			8011	GC-ECD
			8260	GC/MS
tris-(2,3-Dibromopropyl)phosphate	126-72-7	Organic phosphate	8270	GC/MS
Dibutyl phthalate	84-74-2	Phthalate ester	525	GC/MS
			606	GC-ECD
			625	GC/MS
			8060	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS
Dicamba	1918-00-9	Herbicide, chlorophenoxy acid	515.1	GC-ECD
			8150	GC-ECD
Dichlone (Phygon)	117-80-6	Pesticide, chlorinated	8270	GC/MS
trans-1,2-Dichlons ethylene	156-60-5	Halogenated hydrocarbon (VOC)	502.2	GC/PID
			524.2	GC/MS
			601	GC/HSD
			624	GC/MS
			8260	GC/MS
1,2-Dichlorobenzene	95-50-1	Chlorinated hydrocarbon	502.2	GC-ELCD/PID
			524.2	GC/MS
			601	GC-HSD
			602	GC-PID
			612	GC-ECD
			624	GC/MS
			625	GC/MS
			8020	GC/PID
			8120	GC-ECD
			8260	GC/MS
			8270	GC/MS
			OLMO1	GC/MS

(*Continued*)

U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
1,3-Dichlorobenzene	541-73-1	Halogenated hydrocarbon	502.2	GC-ELCD/PID
			524.2	GC/MS
			601	GC-HSD
			602	GC-PID
			612	GC-ECD
			624	GC/MS
			625	GC/MS
			8120	GC-ECD
			8020	GC-PID
			8260	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
1,4-Dichlorobenzene	106-46-7	VOC (halogenated hydrocarbon)	524.2	GC/MS
			601	GC-HSD
			602	GC-PID
			612	GC-ECD
			624	GC/MS
			625	GC/MS
			8020A	GC-PID
			8120	GC-ECD
			8260	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
3,3′-Dichlorobenzidine	91-94-1	Aromatic amine	605	HPLC-EL
			625	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
Dichlorodifluoromethane (CFC-12)	75-71-8	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			8260	GC/MS
1,1-Dichloroethane (ethyledene dichloride)	75-34-3	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
1,1-Dichloroethene (vinylidine chloride)	75-35-4	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
cis-1,2-Dichloroethylene	156-59-2	Halogenated hydrocarbon (VOC)	502.2	GC-ELCD
			524.2	GC/MS
			8260	GC/MS
Dichloroethyl ether	111-44-4	Haloether	611	GC-HSD
			625	GC/MS
			8270	GC/MS
			OLMO1	GC/MS

(*Continued*)

U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
2,4-Dichlorophenol	120-83-2	Phenol	604	GC-ECD/FID
			625	GC/MS
			8040	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS
2,6-Dichlorophenol	87-65-0	Phenol	8040	GC-FID
			8270	GC/MS
1,2-Dichloropropane (propylene dichloride)	78-87-5	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
1,3-Dichloropropane	142-28-9	Halogenated hydrocarbon (VOC)	502.2	GC-ELCD
			524.2	GC/MS
			8260	GC/MS
2,2-Dichloropropane (*sec*-dichloropropane)	594-20-7	Halogenated hydrocarbon (VOC)	502.2	GC-ELCD
			524.2	GC/MS
			8260	GC/MS
1,1-Dichloropropene	563-58-6	Halogenated hydrocarbon (VOC)	502.2	GC-ELCD/PID
			524.2	GC/MS
			8260	GC/MS
cis-1,3-Dichloropropene	10061-01-5	Halogenated hydrocarbon (VOC)	502.2	GC-PID
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			OLMO1	GC/MS
trans-1,3-Dichloropropene	10061-02-6	Halogenated hydrocarbon (VOC)	502.2	GC-PID
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			OLMO1	GC/MS
Dichlorvos (Vapona)	62-73-7	Pesticide, organophosphorus	507	GC-NPD
			8270	GC/MS
Dicrotophos (Bidrin)	141-66-2	Pesticide, organophosphorus	8270	GC/MS
Dieldrin	60-57-1	Chlorinated pesticide	505	GC-ECD
			508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Diethyl phthalate	84-66-2	Phthalate ester	606	GC-ECD
			625	GC/MS
			8060	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS
Diethylstilbestrol	56-53-1	Phenol	8270	GC/MS
Diethyl sulfate	64-67-5	Sulfate ester	8270	GC/MS
Dilantin	57-41-0	Heterocyclic nitrogen compound	8270	GC/MS

(*Continued*)

U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
Dimethoate (Cygon)	60-51-5	Pesticide, organophosphorus	8270	GC/MS
3,3-Dimethoxybenzidine	119-90-4	Aromatic amine	8270	GC/MS
7,12-Dimethylbenz[*a*]anthracene	57-97-6	PAH	8270	GC/MS
N,*N*-Dimethyl-4-(phenylazo) benzenamine	60-11-7		8270	GC/MS
Dimethyl phthalate	131-11-3	Phthalate ester	525	GC/MS
			606	GC-ECD
			625	GC/MS
			8060	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS
2,4-Dimethylphenol	105-67-9	Phenol	604	GC-FID/ECD
			625	GC/MS
			8040	GC-FID/ECD
			8270	GC/MS
			OLMO1	GC/MS
Dinex (2-cyclohexyl-4,6-dinitrophenol)	131-89-5	Nitrophenol	8040	GC-FID
			8270	GC/MS
1,2-Dinitrobenzene	528-29-0	Nitroaromatic	8270	GC/MS
1,3-Dinitrobenzene	99-65-0	Nitroaromatic	8270	GC/MS
1,4-Dinitrobenzene	100-25-4	Nitroaromatic	8270	GC/MS
2,4-Dinitrophenol	51-28-5	Phenol	604	GC-FID/ECD
			625	GC/MS
			8040	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS
2,4-Dinitrotoluene	121-14-2	Nitroaromatic	625	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
2,6-Dinitrotoluene	606-20-2	Nitroaromatic	625	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
Dinoseb	88-85-7	Phenol (nitrophenol pesticide)	515.1	GC-ECD
			8040	GC-FID
			8150	GC-ECD
			8270	GC/MS
Dioctyl phthalate	117-84-0	Phthalate ester	606	GC-ECD
			625	GC/MS
			8060	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS
Dioxin (2,3,7,8-TCDD)	1746-01-6	Dioxin	613	GC/MS
			8280	GC/MS
Diphenylamine (*N*-phenylbenzeneamine)	122-39-4	Aromatic amine	8270	GC/MS
1,2-Diphenyl hydrazine	122-66-7	Azobenzene	8270	GC/MS
Diquat dibromide (Aquacide, Reglone)	85-00-7	Triazine pesticide	549	HPLC-UV
Disulfoton (Disyston)	298-04-4	Pesticide, organophosphorus	507	GC-NPD
			8140	GC-FPD
			8270	GC/MS

(*Continued*)

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Compounds	CAS No.	Type/Class	Method #	Techniques
Disulfoton sulfoxide (oxydisulfoton)	2497-07-6	Pesticide, organophosphorus	507	GC-NPD
Dowicide 6 (2,3,4,6-tetrachlorophenol)	58-90-2	Phenol	8270	GC/MS
Dursban (Chlorpyrifos)	2921-88-2	Pesticide, organophosphorus	508	GC-ECD
			8140	GC-FPD
Endosulfan-I	959-98-8	Pesticide, chlorinated	508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Endosulfan-II (β-endosulfan, thiodan-II)	33213-65-9	Pesticide, chlorinated	508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Endosulfan sulfate	1031-07-8	Pesticide, chlorinated	508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			OLMO1	GC-ECD
Endrin	72-20-8	Pesticide, chlorinated	505	GC-ECD
			508	GC-ECD
			525	GC/MS
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Endrin aldehyde	7421-93-4	Pesticide, chlorinated	508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Endrin ketone	53494-70-5	Pesticide, chlorinated	8270	GC/MS
			OLMO1	GC-ECD
Ethion (Nialate)	563-12-2	Pesticide, organophosphorus	8270	GC/MS
Ethoprophos (Ethoprop)	13194-48-4	Pesticide, organophosphorus	507	GC-NPD
			8140	GC-FPD
Ethyl carbamate	51-79-6	Carbamate pesticide	8270	GC/MS
Ethyl chloride (chloroethane)	75-00-3	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS

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Compounds	CAS No.	Type/Class	Method #	Techniques
Ethylbenzene	100-41-4	VOC (aromatic)	502.2	GC-PID
			524.2	GC/MS
			602	GC-PID
			624	GC/MS
			8020	GC-PID
			8260	GC/MS
			OLMO1	GC/MS
Ethylene dibromide (1,2-dibromoethane, EDB)	106-93-4	VOC (halogenated hydrocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			8011	GC-ECD
			8260	GC/MS
Ethylene dichloride (1,2-dichloroethane)	107-06-2	VOC (halogenated hydrocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
Bis-(2-Ethylhexyl) adipate	103-23-1	Adipate ester	525	GC/MS
Bis-(2-Ethylhexyl) phthalate	117-81-7	Phthalate ester	525	GC/MS
			606	GC-ECD
			625	GC/MS
			8060	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS
Ethyl methanesulfonate	62-50-0	Sulfonate	8270	GC/MS
Famphur (Famophos)	52-85-7	Pesticide, organophosphorus	8270	GC/MS
Fenamiphos (Nemacur)	22224-92-6	Pesticide, organophosphorus	507	GC-NPD
Fensulfothion	115-90-2	Pesticide, organophosphorus	8140	GC-FPD
			8270	GC/MS
Fenthion (Baytex)	55-38-9	Pesticide, organophosphorus	8140	GC-FPD
			8270	GC/MS
Fluoranthene	206-44-0	Polynuclear aromatic hydrocarbon	550.1	HPLC-FL
			610	HPLC-FL
			625	GC/MS
			8310	HPLC-FL
			8270	GC/MS
			OLMO1	GC/MS
Fluorene (9H-fluorene)	86-73-7	Polynuclear aromatic hydrocarbon	525	GC/MS
			550.1	HPLC-UV
			610	HPLC-UV/
			625	GC-FID
			8310	GC/MS
			8270	HPLC-UV
			OLMO1	GC/MS
				GC/MS
o-Fluorophenol	367-12-4	Phenol	8270	GC/MS
Glyphosate	1071-83-6	Pesticide, organophosphorus	547	HPLC-FL

(*Continued*)

U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
Heptachlor	76-44-8	Pesticide, chlorinated	505	GC-ECD
			508	GC-ECD
			525	GC/MS
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Heptachlor epoxide	1024-57-3	Pesticide, chlorinated	505	GC-ECD
			508	GC-ECD
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC/MS
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin	35822-46-9	Dioxin	8280	GC/MS
Hexachlorobutadiene	87-68-3	Halocarbon	502.2	GC-PID/ELCD
			524.2	GC/MS
			612	GC-ECD
			625	GC/MS
			8120	GC-ECD
			8260	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
Hexachlorocyclopentadiene	77-47-4	Halogenated hydrocarbon	505	GC-ECD
			525	GC/MS
			612	GC-ECD
			625	GC/MS
			8120	GC-ECD
			8270	GC/MS
			OLMO1	GC/MS
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin	57653-85-7	Dioxin	8280	GC/MS
1,2,3,4,7,8-Hexachlorodibenzofuran	70648-26-9	Dibenzofuran	8280	GC/MS
Hexachlorobenzene	118-74-1	Halogenated aromatic	505	GC-ECD
			508	GC-ECD
			525	GC/MS
			612	GC-ECD
			625	GC/MS
			8120	GC-ECD
			8270	GC/MS
			OLMO1	GC/MS
Hexachloroethane	67-72-11	Halocarbon	612	GC-ECD
			625	GC/MS
			8120	GC-ECD
			8270	GC/MS
			OLMO1	GC/MS
Hexachlorophene (Nabac)	70-30-4	Phenol	8270	GC/MS
Hexachloropropene	1888-71-7	Chlorinated hydrocarbon	8270	GC/MS
Hexamethylphosphoramide	680-31-9	Phosphoric amide	8270	GC/MS

(*Continued*)

U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
2-Hexanone (methyl butyl ketone)	591-78-6	Ketone	OLMO1	GC/MS
Hydroquinone	123-31-9	Aromatic ketone	8270	GC/MS
Indeno (1,2,3-*cd*)pyrene	193-39-5	Polynuclear aromatic	525	GC/MS
		hydrocarbon	550.1	HPLC-FL
			610	HPLC-FL
			625	GC/MS
			8310	HPLC-FL
			8270	GC/MS
			OLMO1	GC/MS
Isophorone	78-59-1	Ketone	609	GC-FID
			625	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
Isodrin	465-73-6	Chlorinated aromatic	8270	GC/MS
Isosafrole	120-58-1	Benzodioxole	8270	GC/MS
Kepone (chlordecone)	143-50-0	Pesticide, chlorinated	8270	GC/MS
Kerb	23950-58-5	Pesticide, chlorinated amide	507	GC-NPD
			8270	GC/MS
Leptophos (Phosvel)	21609-90-5	Pesticide, organophosphorus	8270	GC/MS
Lindane (γ-BHC)	58-89-9	Pesticide, chlorinated	505	GC-ECD
			508	GC-ECD
			525	GC/MS
			608	GC-ECD
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
Malathion (phosphothion)	121-75-5	Pesticide, organophosphorus	8270	GC/MS
Maleic anhydride	108-31-6	Anhydride	8270	GC/MS
Mesitylene	108-67-8	Aromatic	502.2	GC-PID
			524.2	GC/MS
			8260	GC/MS
Mestranol	72-33-3	Steroid	8270	GC/MS
Metaphos (methyl parathion)	298-00-0	Pesticide, organophosphorus	8140	GC-FPD
			8270	GC/MS
Methapyrilene	91-80-5	Pyridinyl amine	8270	GC/MS
Methiocarb (Mesurol)	2032-65-7	Pesticide, carbamate	531.1	HPLC-FL
Methomyl (Lannate)	16752-77-5	Pesticide, thiocarbamate	531.1	HPLC-FL
Methoxychlor	72-43-5	Pesticide, chlorinated	505	GC-ECD
			508	GC-ECD
			525	GC/MS
			608	GC-ECD
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC-ECD
3-Methylcholanthrene	56-49-5	PAH	8270	GC/MS
Methyl bromide (bromomethane)	74-83-9	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS

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U.S. EPA's Analytical Methods for Organic Pollutants in Aqueous and Solid Matrices (a Partial List)

Compounds	CAS No.	Type/Class	Method #	Techniques
Methyl chloride (chloromethane)	74-87-3	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
2-Methyl-4,6-dinitrophenol	534-52-1	Phenol	604	GC-PID
			625	GC/MS
			8040	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS
Methyl ethyl ketone (2-butanone)	78-93-3	Ketone	OLMO1	GC/MS
Methyl isobutyl ketone (MIBK)	108-10-1	Ketone	OLMO1	GC/MS
Methyl methanesulfonate	66-27-3	Sulfonate ester	8270	GC/MS
2-Methylnaphthalene	91-57-6	PAH	8270	GC/MS
			OLMO1	GC/MS
N-Methyl-*N*-nitrosoethanamine	10595-95-6	Nitrosamine	8270	GC/MS
Methylene bromide (dibromomethane)	74-95-3	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			8260	GC/MS
Methylene chloride (dichloromethane)	75-09-2	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
Metolachlor	51218-45-2	Pesticide, chlorinated	507	GC-NPD
Metribuzin	21087-64-9	Pesticide, triazine	507	GC-NPD
Mevinphos (Phosdrin)	7786-34-7	Pesticide, organophosphorus	507	GC-NPD
			8140	GC-FPD
			8270	GC/MS
Mexacarbate	315-18-4	Pesticide, carbamate	8270	GC/MS
MOCA (4,4′-Methylene-*bis* [2-chloroaniline])	101-14-4	Aromatic amine	8270	GC/MS
Monocrotophos	6923-22-4	Pesticide, organophosphorus	8270	GC/MS
Naled (Dibrom)	300-76-5	Pesticide, organophosphorus	8140	GC-FPD
			8270	GC/MS
Naphthalene	91-20-3	PAH	502.2	GC-PID
			524.2	GC/MS
			550.1	HPLC-UV
			610	HPLC-UV
			625	GC/MS
			8260	GC/MS
			8270	GC/MS
			8310	HPLC-UV
			OLMO1	GC/MS
1,4-Naphthoquinone (1,4-naphthalenedione)	130-15-4	Aromatic ketone	8270	GC/MS
1-Naphthylamine	134-32-7	Aromatic amine	8270	GC/MS
2-Naphthylamine	91-59-8	Aromatic amine	8270	GC/MS

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Compounds	CAS No.	Type/Class	Method #	Techniques
Nicotine	54-11-5	Alkaloid	8270	GC/MS
5-Nitroacenaphthene	602-87-9	Nitroaromatic	8270	GC/MS
2-Nitroaniline (2-nitrobenzenamine)	88-74-4	Nitroaromatic	8270	GC/MS
			OLMO1	GC/MS
3-Nitroaniline	99-09-2	Nitroaromatic (aromatic amine)	8270	GC/MS
			OLMO1	GC/MS
p-Nitroaniline	100-01-6	Aromatic amine (nitroaromatic)	8270	GC/MS
			OLMO1	GC/MS
5-Nitro-*o*-anisidine	99-59-2	Aromatic amine	8270	GC/MS
Nitrobenzene	98-95-3	Nitroaromatic	609	GC-FID
			625	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
4-Nitrobiphenyl	92-93-3	Nitroaromatic	8270	GC/MS
2-Nitrophenol	88-75-5	Phenol	604	GC-FID/ECD
			625	GC/MS
			8040	GC-FID/ECD
			8270	GC/MS
			OLMO1	GC/MS
4-Nitrophenol	100-02-7	Phenol	515.1	GC-ECD
			604	GC-FID/ECD
			625	GC/MS
			8040	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS
4-Nitroquinoline-1–oxide	56-57-5	Heterocyclic nitrogen compound	8270	GC/MS
N-Nitrosodiethylamine	55-18-5	Nitrosamine	8270	GC/MS
N-Nitrosodi-*n*-butylamine	924-16-3	Nitrosamine	8270	GC/MS
N-Nitrosodimethylamine (*N*-methyl-*N*-nitrosomethanamine)	62-75-9	Nitrosamine	625	GC/MS
			8270	GC/MS
N-Nitrosodiphenylamine	86-30-6	Nitrosamine	607	GC-NPD
			625	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
Nitrofen (TOK)	1836-75-5	Chlorinated nitroaromatic	8270	GC/MS
N-Nitrosodi-*n*-propylamine	621-64-7	Nitrosamine	625	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
4-Nitrosomorpholine	59-89-2	Nitrosamine	8270	GC/MS
N-Nitrosopiperidine	100-75-4	Heterocyclic nitrogen compound	8270	GC/MS
N-Nitrosopyrrolidine	930-55-2	Nitrosamine	8270	GC/MS
5-Nitro-*o*-toluidine	99-55-8	Aromatic amine (nitroaromatic)	8270	GC/MS
cis-Nonachlor	5103-73-1	Pesticide, chlorinated	505	GC-ECD
trans-Nonachlor	39765-80-5	Pesticide, chlorinated	505	GC-ECD
			525	GC/MS
Octachlorodibenzo-*p*-dioxin (OCDD)	3268-87-9	Dioxin	8280	GC/MS
Octamethylpyrophosphoramide	152-16-9	Pesticide, organophosphorus	8270	GC/MS

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Compounds	CAS No.	Type/Class	Method #	Techniques
4,4′-Oxydianiline (4,4′-diaminodiphenyl ether)	101-80-4	Aromatic amine	8270	GC/MS
Paraquat	1910-42-5	Pesticide, bipyridinum	549	HPLC-UV
Parathion (Niran)	56-38-2	Pesticide, organophosphorus	8270	GC/MS
1,2,3,7,8,-Pentachlorodibenzo-*p*-dioxin	40321-76-4	Dioxin	8280	GC/MS
1,2,3,7,8-Pentachlorodibenzofuran	57117-41-6	Dibenzofuran	8280	GC/MS
Pentachlorobenzene	608-93-5	Pesticide, chlorinated	8270	GC/MS
Pentachloronitrobenzene	82-68-8	Chlorinated nitroaromatic	8270	GC/MS
Pentachlorophenol	87-86-5	Phenol	515.1	GC-ECD
			525	GC/MS
			604	GC-ECD/FID
			625	GC/MS
			8040	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS
Phenanthrene	85-01-8	Polynuclear aromatic hydrocarbon	525	GC/MS
			550.1	HPLC-FL
			610	HPLC-FL
			625	GC/MS
			8310	HPLC-FL
			8270	GC/MS
			OLMO1	GC/MS
Phenobarbital	50-06-6	Barbiturate	8270	GC/MS
Phenol	108-95-2	Phenol	604	GC-FID/ECD
			625	GC/MS
			8040	GC-ECD
			8270	GC/MS
			OLMO1	GC/MS
Phentermine (1,1-dimethyl-2-phenyl ethanamine)	122-09-8	Aromatic amine	8270	GC/MS
p-(Phenylazo) aniline (aminoazobenzene)	60-09-3	Aromatic amine	8270	GC/MS
Phorate (Thimet)	298-02-2	Pesticide, organophosphorus	8140	GC-FPD
			8270	GC/MS
Phosmet (Imidan)	732-11-6	Pesticide, organophosphorus	8270	GC/MS
Phosphamidon (Dimecron)	13171-21-6	Pesticide, organophosphorus	8270	GC/MS
Phthalic anhydride	85-44-9	Acid anhydride	8270	GC/MS
Picloram	1918-02-1	Pesticide, chlorinated	515.1	GC-ECD
2-Picoline (2-methylpyridine)	109-06-8	Pyridine	8270	GC/MS
Piperonyl sulfoxide	120-62-7	Sulfoxide	8270	GC/MS
Prometon	1610-18-0	Pesticide, triazine	507	GC-NPD
Pronamide	23950-58-5	Amide	515.1	GC-ECD
n-Propylbenzene	103-65-1	VOC (aromatic)	502.1	GC-PID
			524.2	GC/MS
			8260	GC/MS
Propylthiouracil	51-52-5	Organosulfur compound	8270	GC/MS

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Compounds	CAS No.	Type/Class	Method #	Techniques
Pyrene	129-00-0	Polynuclear aromatic hydrocarbon	525	GC/MS
			550.1	HPLC-FL
			610	HPLC-FL
			625	GC/MS
			8310	HPLC-FL
			8270	GC/MS
			OLMO1	GC/MS
Pyridine	110-86-1	Pyridine	8270	GC/MS
Quinone	106-51-4	Aromatic ketone	8270	GC/MS
Resorcinol (1,3-benzenediol)	108-46-3	Phenol	8270	GC/MS
Safrole (1,2-methylendioxy-4-allyl benzene)	94-59-7	Aromatic	8270	GC/MS
Santox (EPN)	2104-64-5	Pesticide, organophosphorus	8270	GC/MS
Silvex (2,4,5-TP)	93-72-1	Chlorophenoxy acid herbicide	515.1	GC-ECD
			8150	GC-ECD
Simazine	122-34-9	Pesticide, triazine	505	GC-ECD
			507	GC-NPD
			525	GC/MS
Stirofos (Rabon, tetrachlorvinphos)	22248-79-9	Pesticide, organophosphorus	507	GC-NPD
			8140	GC-FPD
			8270	GC/MS
Strychnine sulfate	60-41-3	Alkaloid	8270	GC/MS
Styrene (vinylbenzene)	100-42-5	VOC (aromatic)	502.2	GC-PID
			524.2	GC/MS
			602	GC-PID
			624	GC/MS
			8020	GC-PID
			8260	GC/MS
			OLMO1	GC/MS
2,4,5-T	93-76-5	Chlorophenoxy acid herbicide	515.1	GC-ECD
			8150	GC-ECD
2,3,7,8-TCDF (2,3,7,8-tetrachlorodibenzofuran)	51207-31-9	Dibenzofuran	8280	GC/MS
Terbufos (Counter)	13071-79-9	Pesticide, organophosphorus	507	GC-NPD
			8270	GC/MS
1,2,4,5-Tetrachlorobenzene	95-94-3		8270	GC/MS
1,1,1,2-Tetrachloroethane	630-20-6	Halogenated hydrocarbon (VOC)	502.2	GC-ELCD
			524.2	GC/MS
			8260	GC/MS
1,1,2,2-Tetrachloroethane	79-34-5	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
Tetrachloroethylene (perchloroethylene)	127-18-4	Halogenated hydrocarbon (VOC)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS

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Compounds	CAS No.	Type/Class	Method #	Techniques
Tetrachlorophenol	25167-83-3	Phenol	8040	GC-FID
Tetraethylpyrophosphate (TEPP)	107-49-3	Organic phosphate	8270	GC/MS
Thiophenol (benzenethiol, phenyl mercaptan)	108-98-5	Mercaptan	8270	GC/MS
Toluene	108-88-3	Aromatic	502.2	GC-PID
			524.2	GC/MS
			602	GC-PID
			624	GC/MS
			8020	GC-PID
			8260	GC/MS
Toluene-2,4-diisocyanate	584-84-9	Organic isocyanate	8270	GC/MS
o-Toluidine	95-53-4	Aromatic amine	8270	GC/MS
Toxaphene (Camphechlor)	8001-35-2	Pesticide, chlorinated	505	GC-ECD
			508	GC-ECD
			525	GC/MS
			608	GC-ECD
			625	GC/MS
			8080	GC-ECD
			8270	GC/MS
			OLMO1	GC/MS
1,2,3-Trichlorobenzene	87-61-6	VOC (halocarbon)	502.2	GC-ELCD/PID
			524.2	GC/MS
			8260	GC/MS
1,2,4-Trichlorobenzene	120-82-1	Halogenated, aromatic	502.2	GC-ELCD/PID
			524.2	GC/MS
			612	GC-ECD
			625	GC/MS
			8120	GC-ECD
			8260	GC/MS
			8270	GC/MS
			OLMO1	GC/MS
1,1,1-Trichloroethane (methyl chloroform)	71-55-6	Halocarbon	601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
1,1,2-Trichloroethane	79-00-5	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
Trichloroethene	79-01-6	VOC (halocarbon)	502.2	GC-ELCD/PID
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
Trichlorofluoromethane (CFC-11)	75-69-4	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			601	GC-HSD
			8260	GC/MS

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Compounds	CAS No.	Type/Class	Method #	Techniques
(Trichloromethyl) benzene	98-07-7	Chlorinated hydrocarbon	8120	GC-ECD
Trichloronate	327-98-0	Pesticide, organophosphorus	8140	GC-FPD
2,4,5-Trichlorophenol	95-95-4	Phenol	8270	GC/MS
			OLMO1	GC/MS
2,4,6-Trichlorophenol	88-06-2	Phenol	604	GC-ECD/FID
			625	GC/MS
			8040	GC-ECD/FID
			8270	GC/MS
			OLMO1	GC/MS
Trichlorophenol	25167-82-2	Phenol	8040	GC-FID
1,2,3-Trichloropropane	96-18-4	VOC (halocarbon)	502.2	GC-ELCD
			524.2	GC/MS
			8260	GC/MS
1.1,2-Trichloro-1,2,2-trifluoroethane (Freon-113)				
O,*O*,*O*-Triethylphosphorothioate	126-68-1	Pesticide, organophosphorus	8270	GC/MS
Trifluralin (Treflan)	1582-09-8	Pesticide, organofluorine	508	GC-ECD
			8270	GC/MS
2,4,5-Trimethylaniline	137-17-7	Aromatic amine	8270	GC/MS
1,2,4-Trimethylbenzene	95-63-6	Aromatic	502.2	GC-PID
			524.2	GC/MS
			8260	GC/MS
Trimethylphosphate	512-56-1	Organic phosphate	8270	GC/MS
1,3,5-Trinitrobenzene	99-35-4	Nitroaromatic	8270	GC/MS
Trithion (carbofenothion)	786-19-6	Pesticide, organophosphorus	8270	GC/MS
Vancide-89	133-90-4	Pesticide, chlorinated	515.1	GC-ECD
Vinyl chloride (chloroethene)	75-01-4	VOC (halocarbon)	502.2	GC-PID/ELCD
			524.2	GC/MS
			601	GC-HSD
			624	GC/MS
			8260	GC/MS
			OLMO1	GC/MS
Vydate (Oxamyl)	23135-22-0	Pesticide, thiocarbamate	531.1	HPLC-FL
m-Xylene	108-38-3	Aromatic	502.2	GC-PID
			524.2	GC/MS
			8260	GC/MS
o-Xylene	95-47-6	Aromatic	502.2	GC-PID
			524.2	GC/MS
			8260	GC/MS
p-Xylene	106-42-3	VOC (aromatic)	502.2	GC-PID
			524.2	GC/MS
			8260	GC/MS
Xylenes (total xylene)	1330-20-7	Aromatic	8020	GC-PID
			OLMO1	GC/MS
Zinophos (Thionazin)	297-97-2	Pesticide, organophosphorus	8270	GC/MS

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