Laubereau, P. G. (1985): The Status of the Development of Standard Procedures for the Analysis of Organic Priority Pollutants in Water Samples in the Federal Republic of Germany. Paper presented at the Fourth European Symposium – Organic Micropollutants in the Aquatic Environment, Wien, October 22-24,1985. – p. 40-65; Dordrecht (Reidel).

THE STATUS OF THE DEVELOPMENT OF STANDARD PROCEDURES FOR THE ANALYSIS OF ORGANIC PRIORITY POLLUTANTS IN WATER SAMPLES IN THE FEDERAL REPUBLIC OF GERMANY

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SUMMARY

An overview is given about the existing and planned standard methods for the analysis of organic priority pollutants in water samples in the Federal Republic of Germany. The priority pollutants referred here are those of the EEC-List of dangerous substances, issued in 1982.- Taking a proposed standard for "Low Volatile Chlorinated Hydrocarbons" as an example, some of the difficulties and problems which arise in case a method has to be standardized, are discussed.

1. INTRODUCTION

With this lecture I want to present to you a status report about the existing and planned German standard procedures for the determination of organic "priority pollutants". In addition to this I want to discuss some of the problems which arise during the practical realization of a standard. It is hoped that my lecture and a discussion can give to you some stimulation and some awareness about work which needs to be done.

At the beginning please allow that I give some short information about the organization which deals with the standardization of water analysis in Germany and that I explain which kind of "priority pollutants" is discussed here.

1.1 THE ORGANIZATION FOR THE STANDARDISATION OF PROCEDURES FOR WATER ANALYSIS IN GERMANY

The availability of standardized methods is of great importance for the determination of organic micropollutants in water. Only by good harmonization, by an appropriate description of a procedure and by an uniform practice of methods, or at least by a harmonized correlation of the techniques and procedures of analysis to equal criteria of quality and analytical objectives, it is possible to achieve the necessary comparability of results, with regard to parameters measured, matrices, local and temporal necessities and other variables of an environmental investigation.

As shown in figure 1, the standardization of methods for water analysis in Germany is done by a joint operation of the "Deutsches Institut fuer Normung (DIN)" and by the "Fachgruppe Wasserchemie der Gesellschaft Deutscher Chemiker", supported by the federal and the state governements, universities, industry and other groups.

The work is done by the leading committee for the "German standard methods (Deutsche Einheitsverfahren) for examination of water, wastewater and sludge" , its sub-committees and its related working groups.

A compilation of these standards is issued as "Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlamm-Untersuchung" (1), in a loose-bound manner and updated regularely.

1.2 THE WORKING GROUPS FOR THE STANDARDISATION OF METHODS FOR THE ANALYSIS OF ORGANIC COMPOUNDS IN WATER-SAMPLES

The existing working groups for organic compounds are listed in figure 2. As you see the 9 groups cannot cover the whole range of possible organic pollutants and their analysis. It is urgent therefore to expand the number of groups in immediate future.

1.3 THE "PRIORITY POLLUTANTS"

The priority pollutants about which I am talking here are those from the EEC-list of priority pollutants (2).

This is not the place to discuss the completeness and the relevance of this selection of compounds and to make comparisons with other lists of priority pollutants. My task here simply is to give to you a review about standards which are available for a selected variety of highly different organic compounds which are of certain importance to the aquatic environment.

For a general information I have tried to arrange the EEC priority pollutants into groups a shown in figure 3.

2. EXISTING STANDARDS AND STANDARDS UNDER DEVELOPMENT

2.1 METHODS FOR THE DETERMINATION OF AROMATIC HYDROCARBONS AND POLYNUCLEAR AROMATIC HYDROCARBONS (PAH)

2.1.1 METHODS FOR THE DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN DRINKINC WATER

(DIN 38 403 Part 13)

The German standard DIN 38 403 Part 13 includes three procedures, all based on thin layer chromatography (TLC). Their fields of application are:

Procedure 1:	qualitative screening test
Procedure 2:	semi-quantitative screening test (to check if the concentration of PAH exceeds 20% of the threshold value)
Procedure 3:	quantitative determination

Figure 4 presents a flow-diagram of procedure 3.

The standard is very much oriented to the needs of the German "Trinkwasser Verordnung (TVO)". As shown in figure 5 the procedure principally allows for the separate determination of 6 PAH. However for survey purposes with respect to the TVO, the sum of the concentrations of the PAH found, is reported as the result of the analytical determination

2.1.2 DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS WITH HPLC

(Proposal for a DIN 38 407 Part 8)

Since several years efforts are made at the DIN as well as at the ISO (International Standard Organization) to issue a standard for the determination of PAH by high performance liquid chromatography (HPLC). As shown in figure 6 a german proposal includes two HPLC-based procedures, one using an enrichment by extraction and the other an enrichment by adsorption. The proposed standard is very much like the standard proposed in an ISO-Draft (ISO DP 43 of the respective working group (TC 147 WG 19)).

The performance characteristics of this proposal is summarized in figure 7.

At the level of the international standard organization a procedure for the determination of 22 PAH by the HPLC-method is under discussion. This procedure is determined to measure the contents of PAH in all kinds of water, in sediment and in fish. It is an extensive multi-step method using gel-permeation chromatography and alumina column chromatography for clean-up purposes. On demand it would be possible to show to you figures about the procedure and its performance characteristics.

2.1.3 DETERMINATION OF BENZENE AND HOMOLOGUES

(Proposal for a DIN 38 407 Part 7)

The determination of benzene and its homologues, as it is proposed for a standard DIN 38 407 Part 7, is a straightforward gas chromatographic method. The flow diagram is shown in figure 8. The detection occurs via flame ionization detector (FID).

And as shown in figure 9 the method is applicable for the investigation of sewage and effluents.

2.2 PROCEDURES FOR THE DETERMINATION OF HALOGENATED HYDROCARBONS AND ORGANOCHLORINE PESTICIDES

2.2.1 THE DETERMINATION OF VOLATILE HALOGENATED HYDROCARBONS IN WATER SAMPLES

(Proposal for a standard DIN 38 407 Part 4)

A reliable standard for the determination of volatile halogenated hydrocarbons is of special importance for environmental pollution control. It took several years and many discussions to harmonize a procedure. The method which now is in its final stage of elaboration is shown in figure 10. The basic concept is the gas chromatographic analysis with electron capture detector (GC-ECD) after a step of separation and enrichment by extraction. For some of the compounds FID-detection is necessary or recommended.

The performance characteristics of the procedure is summarized in figure 11. As you see, the standard is applicable for all kinds of halogenated hydrocarbons with 1 to 6 carbon atoms. The standard gives rise for a series of questions with respect to the substances determined and the type of sample. These questions I want to postpone for the discussion at the end of my talk and for the comments I will make afterwards with respect to problems which arise if you design a standard. At the moment I want to point on the following :

(-) The necessary, statistically proven, data about the performance of the method (accuracy, yields, precision, limits of detection etc.) have yet to be determined by inter-laboratory comparison. A first round robin test, performed 2 years ago, produced data which could not be interpreted.

(-) The method does not use additional clean-up and enrichment procedures besides the step of extraction.

(-) Concerning a head-space GC-ECD method, the discussion is still going on, if it is necessary and possible for volatile halogenated hydrocarbons to standardize this kind of method in addition to the extraction method, beyond the case of chloroethene which is described in section 2.2.2.

2.2.2 DETERMINATION OF CHLOROETHENE (VINYL CHLORIDE) BY HEAD-SPACE GAS CHROMATOGRAPHY

(Draft DIN 38 413 Part 2)

Because of the properties of chloroethene it was decided to issue a separate standard for this compound based on the head-space technique. The flow diagram of this method is shown in figure 12 and the performance characteristics is summarized in figure 13. The method has yet to be tested by an intercomparison run.

2.2.3 GAS CHROMATOGRAPHIC DETERMINATION OF LOW VOLATILE HALOGENATED HYDROCARBONS AND ORGANOCHLORINE PESTICIDES

(Proposal/"Blaudruck" for a DIN 38 407 Part 2)

For the determination of low volatile halogenated hydrocarbons and organochlorine pesticides a so called "Blaudruck" (blueprint), issued under the responsibility of the working group, is ready now for beeing tested in the public before becoming a definite standard. As I shall talk in a further part of the lecture a bit more about basic problems occuring with the development of standards, using this "Blaudruck"as an example, in the section here I only want to present to you a general information about the procedure, as shown in the figures 14 (flow-diagram), 15 (performance characteristics) and 16 (list of selected compounds).

2.3 PHENOLS

2.3.1 DETERMINATION OF SELECTED PHENOLS BY GAS CHROMATOGRAPHY

(Proposal for DIN 38 407 Part 10)

At this stage of the standardization the basic concept for the determination of phenols from the EEC-list of priority pollutants is the analysis by GC. For some of them like : 2-amino-4-chloro-phenol, 2-chloro-phenol, 3-chloro-phenol and 4-chloro-phenol, their analysis by HPLC is discussed and under consideration for a standard.

The analysis for the determination of phenols by GC according to the proposed standard follows the scheme shown in figures 17 and 17a, the performance characteristics is listed in figure 18 and the compounds wich can be analyzed are shown in fig. 19.

3. PRIORITY POLLUTANTS FOR WHICH, UNTIL NOW, NO STANDARD PROCEDURE IS PROPOSED

3.1 POLAR HALOGENATED ORGANIC COMPOUNDS

This group includes the compounds :

(-) Chloral hydrate
(-) Chloro acetic acid
(-) 2-Chloro ethanol
(-) Epichlorohydrin
(-) 1,3-Dichloropropane-2-ol

First ideas for the analytical concept within a standard are:

(-) the determination of chloro acetic acid by GC via derivatives,
(-) the determination of epichlorohydrin by GC-FID after extraction with chloroform

and

(-) the determination of 1,3-dichlorpropane-2-ol by HPLC

Concerning the epichlorohydrin one should mention that one of the procedures under consideration originally is working with packed columns (stationary phase 1,2,3-tris(2-cyanethoxy)-propane on chromosorb P/AW) and does not give a good limit of detection (about 100 ug/l!). Another proposed procedure is using capillary columns with carbowax as the stationary phase. The main problems are not the GC separation and the detection but the separation and the enrichment from the water phase. Therefore some work must be done to complete and to improve the method with respect to these points.

For chloral hydrate and for 2-chloro ethanol until now no procedure is proposed.

3.2 AROMATIC AND ALIPHATIC AMINES

This group includes the compounds listed in Figure 20. A possible way for the determination seems to be by application of HPLC. First discussions are under way to check if such a procedure would be sufficient for the needs of environmmental pollution control.

3.3 ORGANONITROGEN AND ORGANOPHOSPHOROUS PESTICIDES, AND PHENOXYALKYL ACID HERBICIDES, INCLUSIVE EEC-COMPOUND NO.114 : TRIBUTYLPHOSPHATE

The present situation with respect to a standard procedure concerning the organonitrogen and organophosphorous pesticides as well as with the phenoxyalkyl acid herbicides is similar to the situation with the search for an appropriate procedure for the aromatic and aliphatic amines. A definite proposal for a standard does not exist. There is a certain tendency now to consider the HPLC as one possible method for the determination.

The compounds under consideration here are listed in figure 21. For another group, listed in Figure 22, a standard based on GC-analysis may be developed one day.

Concerning the phenoxyalkyl acid herbicides an old and very preliminary proposal, alternative to the HPLC-concept, with a gas chromatographic procedure, already exists, as follows:

The phenoxyalkyl acid pesticides are extracted from the water sample with acetic acid ethyl ester. After derivatization under nitrating conditions and esterification with methanol/ sulfuric acid, and after a clean-up with an alumina column, the derivatives are analyzed with GC/ECD. The limit of detection is in the range of 0.5 ug/l, applying packed column techniques.

3.4 ORGANOTIN COMPOUNDS

For the group of those eight positions of the EEC-list of priority pollutants which concern the organotin compounds it is planned to develop a standard with a HPLC-method for their determination. Naturally, at this stage of the discussion one also is evaluating the advantages of a gas chromatographic procedure as alternative.

4. PROBLEMS ARISING WITH THE STANDARDISATION OF PROCEDURES FOR THE DETERMINATION OF ORGANIC MICROPOLLUTANTS

4.1 GENERAL REMARKS

The first question is : Do we need standard procedures?

If we affirm this question, the second question arises : How does an ideal standard for organic micropollutants look like?

The working group for the development of a standard for the "determination of low volatile chlorinated hydrocarbons and organochlorine pesticides" has had many discussions about these questions and in the following I want to report about some aspects and some of the results of this group in which I am working (3). We think that we have made some progress in answering these questions, although we are far from having solved every problem.

To our opinion the first question can be definitely answered with : YES, and the reason for this can be given in a short way as follows :

A modern concept of analytical quality assurance, as it is practised for instance by the WHO global environmental monitoring program and as it was originally proposed by a group of the Water Research Centre in Medmenham/England (4), includes the following parts :

1. establish working group
2. define objects
3. chose analytical methods
4. >> ensure unambigious description of methods <<
5. estimate within laboratory precision
6. set up control charts
7. compare calibration standard solutions
8. check inter-laboratory bias

As you see the unambigious description of the analytical method is essential part of the analytical quality assurance. We think the adequate described standard procedure, which in addition to this must be thoroughly practically proven, is the proper means of fulfilling this requirement.

On the one hand it cannot be the task of every single laboratory to develop and to describe its own procedure, on the other hand it is clear to everyone working in the field of environmental routine analysis of organic micropollutants, that even if the basic and essential quality data of a laboratory method, - like : accuracy, reproducibility or yields - , are known, the equivalency and comparability of results coming from different laboratories can be improved if methods as uniform as possible are applied.

In this respect I have to hint especially on the following points and problems :

- The many steps and the complexicity of the methods involved!
- The question : which steps are included in the method and in the evaluation of the quality data?
- The individual and often changing composition of environmental samples!

This leads to the discussion and the answering of the second question.

4.2 DISCUSSION OF SELECTED PROBLEMS AND REQUIREMENTS IN CONNECTION WITH THE DEVELOPMENT OF A STANDARD METHOD

(Shown by example of the proposed standard for the determination of low volatile halogenated hydrocarbons and organochlorine pesticides (5))

On principle there exists always a great manyfold of requirements, objectives and limitations which must be considered if one develops a standard procedure. The available time for this lecture is not enough to present to you a systematic and exhausting overview with respect to this. It might be worth trying it one day at another opportunity because the experience shows that gaining of these necessary informations often is neglected.

Today I want to stress some selected points, especially those requirements which gave rise for problems during the development of a standard for the determiniation of low volatile halogenated hydrocarbons and organochlorine pesticides. From this you will see, among others, that there is or may be a distinct difference between a procedure which a single laboratory is developing in a straightforward manner for its very special own needs and the standard which has to satisfy a (possibly) broad range of needs and applications.

I am emphasizing this very much because there is often a lack of comprehension between scientists and legislators if it takes some while to issue a harmonized standard procedure for the determination of certain parameters despite the fact that some analysts and some laboratories are already able to detect and to quantify these parameters in some of the samples under consideration.

The standard to which I am refering now was already discribed in its outline in part 2.2.3 of this lecture.Therefore

I can step directly into the discussion of the problems :

Problem No.1: Which substances shall be determined?

The group of low volatile chlorinated hydrocarbons and organochlorine pesticides includes a nearly innumerable quantity of compounds. From this it is not feasable to publish a separate standard for each compound (like it is the case for chloroethene) or even for a greater number of subgroups of compounds. On the other hand it seems very risky to issue a standard which, without restrictions, allows the determination of all the respective substances.

Therefore it was decided that the standard discussed here can be applied on principle for the whole group of compounds under consideration. However by the editing working group the standard is tested explicitly only for about 25 - 30 representative compounds, which are of : special interest, of special importance and of different types of chemical structure, physical behaviour and analytical detectability. For this group of compounds the standard assumes a particular "analytical responsibility".

If an analyst has the task of analyzing for other compounds of the group of low volatile halogenated hydrocarbons and organochlorine pesticides, beyond the list of 25 - 30 substances,

(-) he is obliged to apply this standard, with its instructions, with the respective instrumentation, with the criteria, etc., mentioned therein,

however

(-) he has to proof the feasability of the procedure with respect to the new compounds, in a thorough and responsible manner, before analyzing samples.

A special problem was the treatment of the" PCB-question". About this I will report in a separate section of my lecture.

(Remark : Concerning the complementary standard for the volatile halogenated hydrocarbons, as described before, to my opinion these borderlines are not drawn so clear!)

Problem No. 2: Which type of sample is allowed?

The question arose if different standard methods should be developed for different types of samples, like drinking water, surface water, or sewage? The result of extensive discussions was, that in many practical cases and from the analytical point of view it is difficult to make a sharp and unequivocal distinction between the different kinds of samples.

Therefore ist was decided to cover with this standard all possible types (matrices) of samples and simply to distinguish between:

Group 1:	water with no or low pollution (normally drinking water, ground water, certain surface waters)
Group 2:	water with moderate pollution (certain surface waters)
Group 3:	heavily polluted water (sewage and certain effluents; certain ground water)

in connection with the effort necessary for using clean up procedures and for the confirmation of the results.

It remains to the responsibily of the analyst to adjust his analytical efforts in a proper way to the sample which has to be analyzed and to prove the feasability of the method by checking carefully a set of necessary characteristic data for the procedure (e.g. separation quality of columns, yields, limits of detection, repeatability and so on).

Problem No. 3: The Identification and the confirmation of the qualitative result

Prerequisite for the determination of a compound is the unequivocal identification. Many thoughts had to be devoted to the problem of adequate ways of identification, because there were no rules available from other sources. Without going into details the following are the outlines of our concept:

1. The analytical effort has to be adjusted to the problem to be solved.
2. The quality of separation efficiency of the columns used must be checked and proven to fulfill certain (minimum) needs (Remark : in most cases capillary column techniques has to be applied).
3. For an adequate confirmation of a result the gas chromatographic evidence of a compound, obtained with at least two columns of different polarity, is mandatory.
4. Different stages of the degree of identification and confirmation are formulated:
   (-) not identified (if no peak appears in case of analyzing only with one GC-column)
   (-) identity possible (if a peak with the expected retention time appears in case of analyzing with one GC-column)
   (-) identity very likely (if corresponding peaks appear at gas chromatograms of two columns of different polarity)
   (-) identity confirmed/ensured (in case of group 1 and group 2 samples identity confirmed if corresponding peaks appear at gas chromatograms of two columns of different polarity; in case of group 3 samples further confirmation, e.g. 3rd column or GC/MS identification may be necessary, depending in the problem to be solved.)
5. Together with the quantitative results, the analyst has to report about the degree of identification/confirmation (including an information about the quality of separation and clean-up).

Problem No. 4: The ways of calibration and of calculation of the result

There may be many reasons for getting wrong results. However one source for doubtful or incomperable results, which very often is neglected, is an inadequate or obscured way for calibration and calculation of the results.

With respect to the different objectives for an analysis and to the considerable analytical effort which possibly is necessary, it was decided to offer within the standard the possibility for a problem-oriented choice of options for calibration and calculation of results. Within this frame the aspects of :

- (-) single-point-calibration
- (-) multiple-point-calibration (at least 5 points)
- (-) standard addition
- (-) internal standardisation
- (-) external standardisation
- (-) calibration including the total procedure
- (-) calibration not including the total procedure
- (-) correction of the result by typical yields and by background
- (-) calibration with linear and with non-liniar calibration functions

are treated. The different possibilities are described separately and the analyst can use them according to his needs. However he is obliged to cite the way of his procedure together with the results.

<u>Problem No. 5: The general concept, the structure and the volume of the standard</u>

From the discussion of problems 1 trough 4 you probably feel that the question about a general concept, the structure and the extent of the contents of the standard had to be solved. As a result of many considerations, especially with respect to

- (-) the optimization of the analytical effort

and to

- (-) an optimized quality of the analytical result

the over-all concept is the following:

> The standard provides and describes all necessary steps for the identification and determination of the compounds in different kinds of samples. In addition to this it provides, if necessary, minimum requirements and instructions for the check and the control of the procedure.

This leads to the structure of a standard with "analytical modules" which can be used according to the needs. For instance concerning the clean-up the following methods are options :

- (-) Separation with acetonitrile
- (-) column chromatography with Florisil
- (-) column chromatography with alumina
- (-) column chromatography with silica

Concerning gas chromatographic separation capillary column techniques is very much recommended, although, for certain purposes, packed column techniques is considered as an option.

It was decided to describe the "analytical modules" as detailed as possible and in a way that they can be cited by the analyst. The analyst on the other hand if he uses the standard is obliged to report with the result in a detailed manner about :

- (-) the steps used with the procedure,
- (-) the characteristic data of his selected procedure and/or about the verification of typical performance data (including ways of calibration, calculation, identification as mentioned before)

Problem No 6: The confirmation of the practical feasability of the new standard

The reason that the proposed standard is at the moment at the so called stage of a "Blue print (Blaudruck)" is based in the fact that one felt that it is necessary to carefully check the practical applicability of a standard with a broad field of application, concerning compounds, samples, concentrations, objectives of investigation and so on. To test the proposed standard an extensive 3 year program on the base of inter-laboratority tests was started .

In a first round of experiments the following was checked:

- (-) The multiple point calibration of the GC-step with own and independent standard solutions (compounds: 1,2,3,4-tetrachlorobenzene, HCB, gamma-HCH, PCB-180, beta-endosulfane, endrine, p,p'-TDE),
- (-) the determination of compounds in a sample of pure water to which the compounds mentioned before were added,
- (-) the constancy of the retention time in connection with the degree of identification.

First results of the determination of HCB (52.0 ng/l), beta-endosulfane (204.8 ng/l) and PCB-180 (117.5 ng/l), obtained with non-polar and polar columns, with standard solutions of own or independent origin, show that :

- (-) a recovery between 93 and 104 % can be obtained,
- (-) the inter-laboratory coefficient of variation can be assumed to be better then 15 %,
- (-) tested with HCB the inter-laboratory coefficient of variation is slightly better in case of multiple point calibration compared to a single point evaluation.

Problem No. 7: The "PCB Problem"

The question of an unequivocal, accurate and comparable determination of polychlorinated biphenyls (PCB) and the implementation of a procedure into a standard was, and still is, object of many discussions of the working group. The status now is the following :

1.) Among the following possible alternatives for a PCB-analysis :
   a.) determination of the total contents of PCB after per-chlorination,
   b.) determination of the total contents of PCB after de-chlorination,
   c.) determination by packed-column GC,
   d.) determination of, or via single compounds by capillary column GC,
   only the case d.) will be part of a standard.
2.) As there are different objectives for the determination of PCB, like :
   a.) to get an information about products (e.g. concentration of Aroclor 1260 etc.)
   b.) to get an information about the sum of PCB (e.g. total contents of PCB)

c.) to get an information about single components (e.g. concentration of 2,2'-dichlorobiphenyl etc.)

it seems necessary to provide separate procedures.

3.) It was decided finally to offer the following three options and analytical procedures, either in a separate standard or in an appendix to the standard for low volatile halogenated compounds :

- a.) The determination of 6 (to 10?) "indicator PCB". (The procedure is more or less the procedure al ready given by the proposed standard for low-volatile halogenated compounds. It follows the concept of "indicator PCB" which is under discussion at other groups (6)(7)(8)(9). The indicators are the PCB 28, 52, 101, 138, 153, 180 (according to the systematic numbering of Ballschmiter (10))).
- b.) The identification, determination and comparison of patterns of products.
  No final decision is made until now with respect to the pattern recognition procedure although there are some models under tentative consideration.
- c.) The unequivocal identification and determination of a single PCB in special (industrially polluted) samples
  This method uses the mass-spectrometry for identification, confirmation and determination.

5. Final remarks

With this lecture I hope that by directly and indirectly pointing on deficits I gave some stimulations especially to those who have the knowledge and the possibility for the development of suitable analytical methods.

To my opinion one has to promote and to improve the following :

1.) The formation of new working groups.
With this respect in Germany working groups for the
- (-) determination of polar, water soluble organic compounds (e.g. chloroethanol, chloral hydrate, epichlorohydine),
- (-) determination of polymer, water soluble organic compounds (e.g. polyamides, polysaccarides),
- (-) GC determination of organohalogenic compounds which cannot be determined by ECD detection (e.g. chlorobenzene, chlorinated ethers, dichloromethane, 1,2-dichloroethane) however by e.g. Hall detectors or MS,
- (-) GC determination of organophosphorous and organonitrogen compounds,
- (-) determination of adsorbable organic sulfur compounds,

are planned.

2.) The participation of a greater number of experienced analysts in the production of standards.

3.) Better and more precise objectives for the projects of standardisation.

4.) Production of standards which are true laboratory procedures. This means complete methods according to which analytical work can be done. Procedures which consider and treat all the relevant problems and cases of application, and last but not least procedures with suitable information about characteristic data. In this respect it is necessary to reach agreement in many important details, for instace about the questions
(-) What shall be summarized under the term "analytical procedure"?
or
(-) what is the definition of the "limit of detection" of an analytical procedure?
and so on....

With these questions let me finish, thanking you very much for your attention.

REFERENCES

(1) DEUTSCHE EINHEITSVERFAHREN ZUR WASSER-, ABWASSER- UND SCHLAMM-UNTERSUCHUNG, Herausgegeben von der Fachgruppe Wasserchemie in der Gesellschaft Deutscher Chemiker, VCH Verlags GmbH, Weinheim

(2) Mitteilung der Kommission an den Rat ueber die gefaehrlichen Stoffe im Sinne der Liste 1, Amtsblatt der Europaeischen Gemeinschaften Nr.C 176/3 vom 14.7.82

(3) P.G.LAUBEREAU, Zum Stand der Normung eines Verfahrens fuer die Bestimmung von schwerfluechtigen Halogenkohlenwasserstoffen und Organochlorpestiziden in Wasser, Korrespondenz Abwasser, 31, 499 - 508 (1984)

(4) UNEP/WHO/UNESCO/WMO Project on Global Water Quality Monitoring, GEMS/WATER Operational Guide, Charpter IV, Analytical Quality Control (Prepared in cooperation with the Water Research Centra Medmenham Laboratory, Medmenham-Marlow, Buckinghamshire, England)
World Health Organization Document ETS/78,9

(5) P.G.LAUBEREAU et al., Vorschlag fuer ein Deutsches Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, gemeinsam erfassbare Stoffe (Gruppe F), Gas-chromatographische Bestimmung von schwerfluechtigen Halogenkohlenwasserstoffen und Organochlorpestiziden in Wasser (F 2), Deutsche Einheitsverfahren (DEV), 14. Lieferung 1985, VCH Verlag GmbH, Weinheim

(6) H.BECK und W.MATHAR, Analysenverfahren zur Bestimmung von ausgewaehlten PCB-Einzelkomponenten in Lebensmitteln, Bundesgesundheitsblatt, 28, 1 (1985)

(7) M.CARL, Hrsg., Rahmenkonzept fuer die Routineanalytik von polychlorierten Biphenylen (PCB), Manuskript erarbeitet von der Arbeitsgruppe "Organische Spurenanalytik", VDLUFA-Schriftenreihe, Heft 12, VDLUFA-Verlag, Darmstadt, 1985, ISBN 3-922712-11-6

(8) L.G.M.TH.TUINSTRA, A.H.ROOS and G.A.WERDMUELLER, BCR-Ringtest of individual chlorobiphenyls (2/1983) - Summary of results (A concept), EC-Report 84.27, Buereau of Reference, Brussels, (1984)

(9) COST 681, Working Party 2, Laboratories Intercomparison on PCBs in Sewage Sludges (1983 - 1984), Meeting, Langen (FRG), 20-21 march 1985

(10) K.BALLSCHMITER und H.J.ZELL, Analysis of Polychlorinated Biphenyls (PCB) by Glas Capillary Gas Chromatography, Fres. Z. Anal. Chem. 302, 20 (1980)

Figure 1

THE ORGANIZATION FOR THE STANDARDIZATION OF PROCEDURES FOR WATER ANALYSIS IN GERMANY

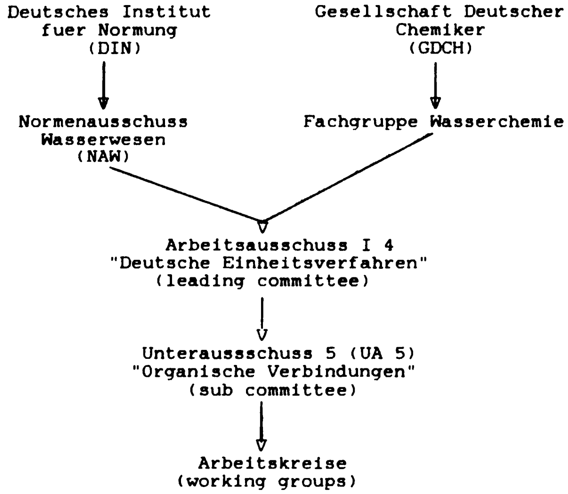


Figure 2

THE EXISTING WORKING GROUPS (WG) FOR THE STANDARDIZATION OF PROCEDURES FOR THE ANALYSIS OF ORGANIC COMPOUNDS IN WATER SAMPLES

WG 1	Polyaromatic hydrocarbons (PAH)
WG 2	Volatile chlorinated hydrocarbons (VCH)
WG 3	Low volatile chlorinated hydrocarbons (LVCH)
WG 4	Phenolic compounds analyzed with GC (Ph-GC)
WG 5	Organic compounds analyzed with HPLC (OC-HPLC)
WG 6	Benzene (Bz)
WG 7	Chloroethene / Vinylchloride (VC)
WG 8	Nitrilo-tri-aceticacid (NTA)
WG 9	Carbondisulphide (CS2)

Figure 3

ATTEMPT OF A GROUP-ARRANGEMENT OF THE ORGANIC "PRIORIY POLLUTANTS" OF THE EEC-LIST

---

1. Aromatic hydrocarbons, including polyaromatic hydrocarbons (PAH)
2. Halogenated hydrocarbons and organochlorine pesticides
    - (-) volatile halogenated hydrocarbons
    - (-) low-volatile halogenated hydrocarbons (including nitrated compounds)
    - (-) organochlorine pesticides
3. Phenols
4. Polar halogenated organic compounds
5. Aromatic and aliphatic amines
6. Organonitrogen and organophosphorous pesticides, inclusive phenoxyalkyl acid herbicides and EEC-No. 114 tributylphosphate
7. Organometallic compounds of tin

Figure 4

DETERMINATION OF PAH IN DRINKING WATER ACCORDING TO DIN 38 409 PART 3

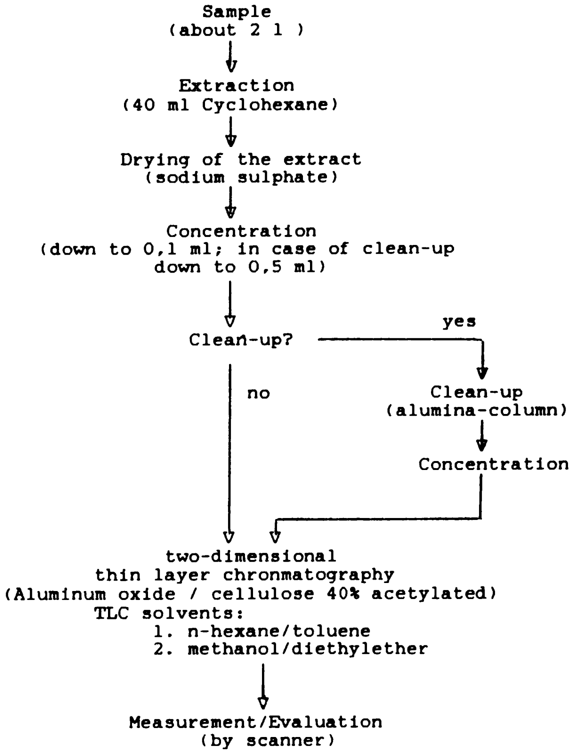


Figure 5

PERFORMANCE CHARACTERISTICS OF THE STANDARD DIN 38 409 PART 3

(DETERMINATION OF PAH IN DRINKING WATER)

SUBSTANCES DETERMINED / RANGE OF APPLICATION

Substance	Range of concentration (ng/l; sample 2 l)
Fluoranthene	5 - 500
Benzo(b)fluoranthene	1 - 250
Benzo(k)fluoranthene	1 - 250
Benzo(a)pyrene	1 - 250
Benzo(ghi)perylene	1 - 250
Indeno(1,2,3-cd)pyrene	2,5- 250

TYPE OF SAMPLE

Drinking water or water with low degree of pollution

CALIBRATION

(-) "2-point-calibration"/external standard
(-) calibration not including the total procedure

IDENTIFICATION

"fixed"/not dependant on the type of sample

Figure 6

DETERMINATION OF PAH BY HPLC

(According to the proposol for a DIN 38 407 Part 8)

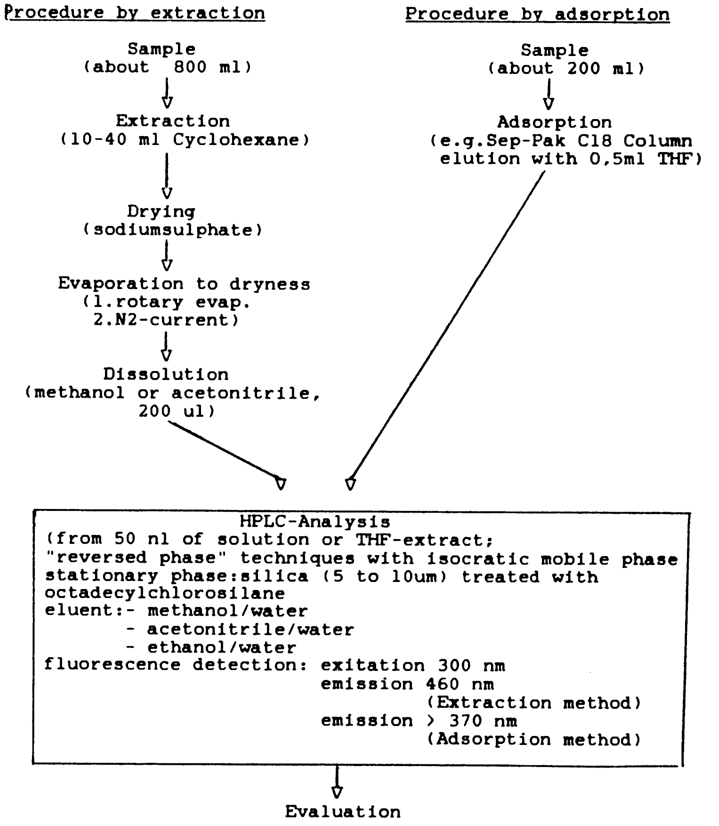


Figure 7

PERFORMANCE CHARACTERISTICS OF THE PROPOSAL FOR A DIN 38 407 PART 8 (HPLC-PROCEDURE)

SUBSTANCES DETERMINED/RANGE OF APPLIKATION:

Substance	Range of concentration	
	Extraction	Adsorption
Fluoranthene	100 ug/l	500 ug/l
Benzo(b)fluoranthene	1-40 ug/l	100 ug/l
Benzo(k)fluoranthene	1-40 ug/l	100 ug/l
Benzo(a)pyrene	20 ug/l	100 ug/l
Benzo(g,h,i)perylene	20 ug/l	100 ug/l
Ideno(1,2,3-c,d)pyrene	20 ug/l	100 ug/l

TYPE OF SAMPLE

Drinking water, ground water, surface water moderately polluted (samples analyzed without filtration)

CALIBRATION

(-) "6-point-calibration"/external standard
(-) calibration not including the total procedure

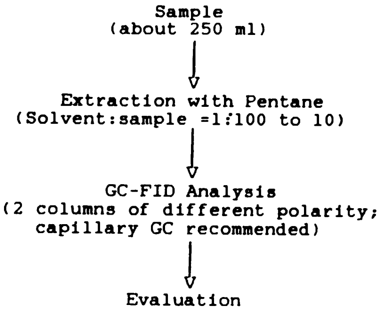
FURTHER CHARACTERISTIC DATA

yet to be determined by inter-laboratory comparison

Figure 8

THE DETERMINATION OF BENZENE AND HOMOLOGUES

(According to the proposal for DIN 38 407 Part 7)



Sample
(about 250 ml)

Extraction with Pentane
(Solvent:sample =1:100 to 10)

GC-FID Analysis
(2 columns of different polarity;
capillary GC recommended)

Evaluation

Figure 9

PERFORMANCE CHARACTERISTICS OF THE PROPOSED-PROCEDURE FOR THE DETERMINATION OF BENZENE AND HOMOLOGUES

(Proposal for a DIN 38 407 Part 7)

SUBSTANCES DETERMINED / RANGE OF APPLICATION:

Substance		Range of concentration (sample size 250 ml)
Benzene	>	1 ng/l to 10 mg/l
Toluene	>	
Xylene	>	
Ethylbenzene	>	
(Isopropyl benzene)	>	
(Biphenyl)	>	

TYPE OF SAMPLE

Water of all kinds, including sewage and effluents

CALIBRATION

(-) multiple point calibration/external standard
(-) Calibration not including the total procedure

RECOVERY

controlled by internal standard (toluene d8?)

IDENTIFICATION

(-) Philosophy: 2 columns of different polarity
(-) if necessary special detector like photo-ionization detector

---

Figure 10

THE DETERMINATION OF VOLATILE HALOGENATED HYDROCARBONS IN WATER SAMPLES

(According to draft DIN 38 407 Part 4)

Sample
(200 ml)

↓

Extraction with Pentane (alt.hexane,o-xylene)
(2-10 ml in case of drinking-or surface water
50 ml in case of effluents)

↓

Drying with Sodiumsulphate
(mantadory in case of o-xylene as solvent))

↓

GC-ECD-Analysis *)
(2 columns of different polarity;
according to objective capillary GC
or packed-column GC)

↓

Evaluation

Remarks: *) dichloro methane, aliphatic mono-chlorinated hydrocarbons and difluoro hydrocarbons with GC-FID

Figure 11

Performance Characteristics of the Procedure for the Determination of High-Volatile Halogenated Hydrocarbons

·(according to the proposal for the standard DIN 38 407 Part 4)

SUBSTANCES DETERMINED :

- fluorinated, chlorinated, bromated and iodated, mainly non-aromatic hydrocarbons with 1 to 6 carbon atoms
- halogenated hydrocarbons with boiling points from 20 to 180 C
- about 24 compounds from the EC-list of priority pollutants

TYPE OF SAMPLE

- groundwater, drinking water, surface water, sewage , effluents

RANGE OF APPLICATION :

- not definitively defined
- depending on compound and sample from about 1 to 100 ug/l

CALIBRATION :

- 6-point calibration with the options :
  - -- calibration including or not including the total procedure
  - -- calibration with external standard or calibration with additional internal standard

STANDARD DEVIATION :

- inter-laboratory precision VR : 20 - 50 % in synthetic sample,depending on conc. and compound

RECOVERY :

- 40 - 90 % after the first extraction, dep. on compound

IDENTIFICATION / CONFIRMATION :

- Philosophy : two columns with different polarity, under certain circumstances conductivity detector or coulometric detector

---

Figure 12

DETERMINATION OF CHLOROETHENE (VINYL CHLORIDE) BY HEADSPACE GAS CHROMATOGRAPHY

(Draft DIN 38 413 Part 2)

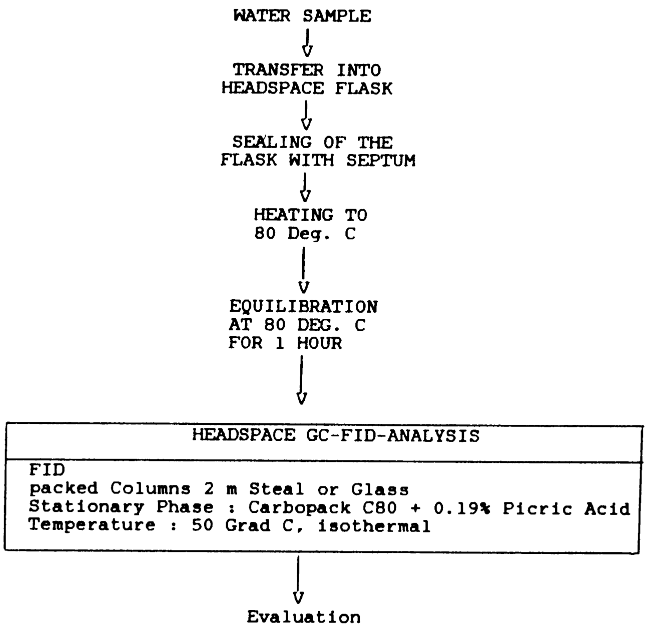


Figure 13

PERFORMANCE CHARACTERISTICS OF THE PROCEDURE FOR THE DETERMINATION OF CHLOROETHENE-(VINYLCHLORIDE)-BY HEADSPACE GAS CHROMATOGRAPHY

(Draft DIN 38413 Part 2)

SUBSTANCES DETERMINED

(-) CHLOROOETHENE (VINYL CHLORIDE)

TYPE OF SAMPLE

(-) all kinds of water samples

RANGE OF APPLICATION

(-) for concentrations of 5 to 500 ng/l

CALIBRATION

Two options:

(-) external 5-point calibration
(-) calibration by standard addition to the sample

STANDARD DEVIATION / RECOVERY

(-) Data to be determined by intercomparison runs

IDENTIFICATION/CONFIRMATION

(-) method as described delivers sufficiently unequivocal results

---

Figure 14

Gas-chromatographic Determination of Low-volatile Chlorinated Hydrocarbons and Organochlorine Pesticides

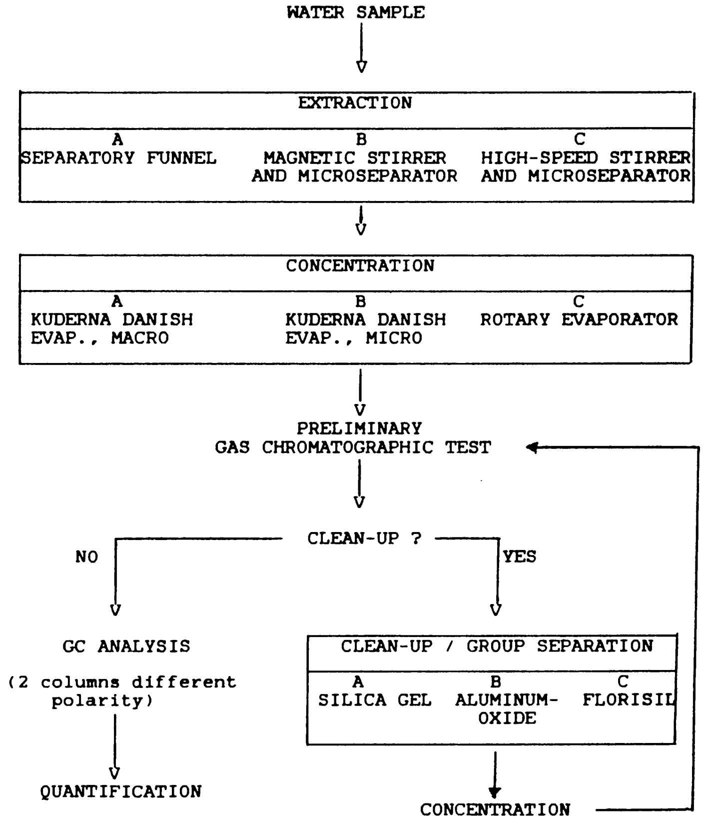


Figure 15
Part 1

PERFORMANCE CHARACTERISTICS OF THE PROCEDURE FOR THE GAS -CHROMATOGRAPHHIC DETERMINATION OF LOW-VOLATILE CHLORINATED HYDROCARBONS AND ORGANOCHLORINE PESTICIDES

(Proposal "Blaudruck" for a DIN 38 407 Part 2)

SUBSTANCES DETERMINED:

(-) acyclic or carbocyclic hydrocarbons with more than 5 carbon atoms; hydrogen atoms substituted by halogens (the NO2-group may be present); vapor pressure at 20 deg. C 10 exp-3 mbar; boiling point < 180 deg. C;

(-) Organochlorine pesticides like DDT and structural related compounds; or compounds derived from hexachlorocyclopentadien (e.g. cyclodien-insecticides); including oxygen and sulfur contaning compounds of this group of pesticides

(-) 27 compounds named, for which the valitity of the procedure is especially checked (among these 13 positions/compounds of the ECC-list of priority-list of priority pollutants)

(-) however in principle applicable for about 24 compounds / "positions" from the ECC-list of priority pollutants

(-) basic procedure for about 7 "PCB-indicator compounds"

Figure 15
Part 2

PERFORMANCE CHARCTERISTICS OF THE PROCEDURE FOR THE GAS-CHROMATOGRAPHIC DETERMINATION OF LOW -VOLATILE CHLORINATED HYDROCARBONS AND ORGANOCHLORINE PESTICIDES

(Proposal "Blaudruck" for a DIN 38 407 Part 2)

TYPE OF SAMPLE

(-) all kinds of water including ground water, surface water, effluents und sewage

RANGE OF APPLICATION

(-) not definitely defined
(-) depending on compound and sample, from about 1 or 10 to 1000 ng/l

CALIBRATION:

(-) various options :

- (- -) "single point calibration"
- (- -) multiple point calibration
- (- -) calibration by standard addition
- (- -) calibration including or not including the total procedure
- (- -) calibration with external standard or calibration with additional internal standard

STANDARD DEVIATION / RECOVERY

(-) data to be determined by intercomparison runs

IDENTIFICATION / CONFIRMATION

Philosophy: (-) analysis with two columns of different polarity is minimum requirement for identification

(-) the degree of the identification of a compound must be reported with the result

(-) in certain cases confirmation of the identifaction with GC/MS

Figure 16

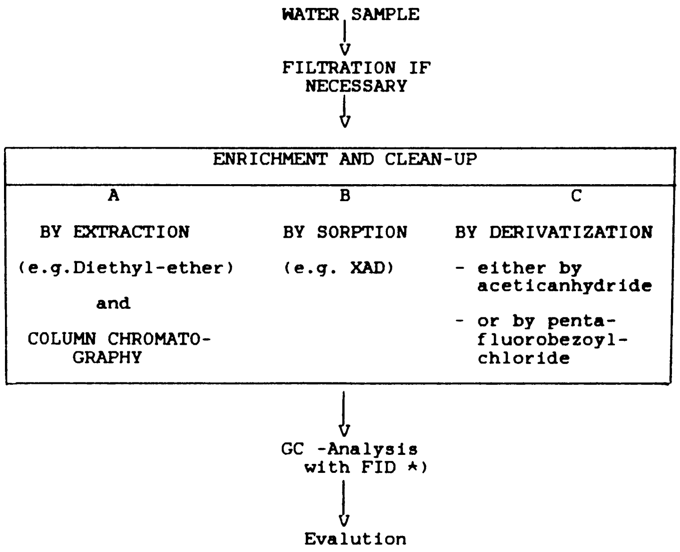
SELECTED COMPOUNDS FOR WHICH THE VALIDITY OF THE PROCEDURE : "PROPOSAL DIN 38 407 PART 2", WILL BE CHECKED

EEC-No.	Substance	EEC-No.	Substance
1	Aldrin	-	Methoxychlor
46	p,p'-DDD (TDE)	-	Pentachlorobenzene
46	p,p'-DDE	-	Pentachloronitrobenzene (PCNB, Quintocene)
46	o,p'-DDT	101	2,4,4'-Trichlorobiphenyl (PCB No.18)
46	p,p'-DDT	101	2,2',5,5'-Tetrachlorobiphenyl (PCB No.52)
71	Dieldrin	101	2,2',4,5,5'-Pentachlorobiphenyl (PCB No.101)
76	alpha-Endosulfan (alpha-Thiodan)	101	2,2',3,4,4',5-Hexachlorobiphenyl (PCB No.138)
76	beta-Endosulfan (beta-Thiodan)	101	2,2',4,4',5,5'-Hexaxchlorobiphenyl (PCB No.153)
77	Endrin	101	2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB No.180)
82	Heptachlor	101	2,2',3,3',4,4',5,5'-Octachlorobiphenyl (PCB No.194)
82	Heptachlorepoxide	109	1,2,4,5-Tetrachlorobenzene
83	Hexachlorobenzene (HCB)	118	1,2,4-Trichlorobenzene
85	alpha-Hexachlorocyclohexane (alpha-HCH)		
85	beta-Hexachlorocyclohexane (gamma-HCH)		
85	gamma-Hexachlorocyclohexane (gamma-HCH) (Lindan)		

Figure 17

GAS -GROMATOGRAPHIC DETERMINATION OF PHENOLS

(According to a proposal for a standard DIN 38 407 Part 10)

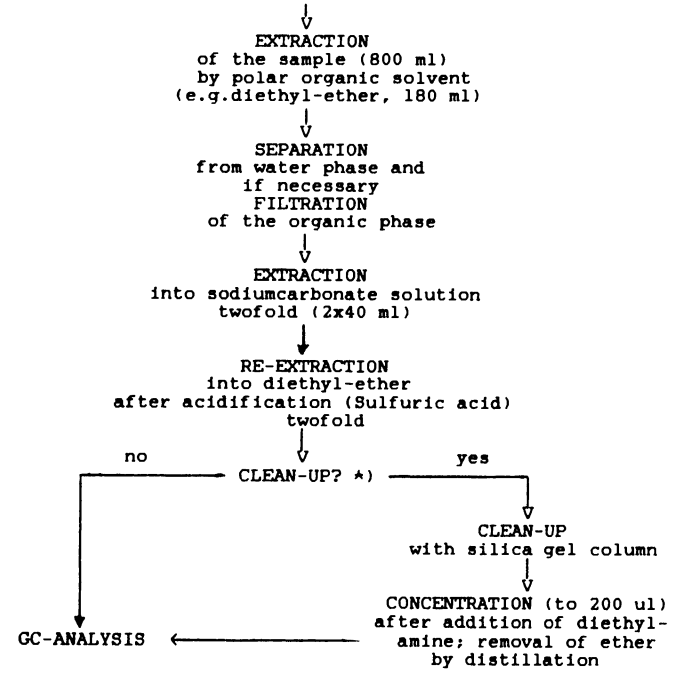


Remarks: *) ECD or MS in certain cases

Figure 17a

GAS CHROMATOGRAPHIC DETERMINATION OF PHENOLS

(here : SCHEME OF THE STEP "ENRICHMENT BY EXTRACTION AND CLEAN-UP",Proposal DIN 38 407 Part 10)



Remarks : *) necessary in case of heavy polluted samples

budal0

Figure 18

PERFORMANCE CHARACTERISTICS OF THE PROCEDURE FOR THE GAS CHROMATOGRAPHIC DETERMINATION OF PHENOLS

(According to a proposal for a standard DIN 38407 part 10)

SUBSTANCES DETERMINED

(-) PHENOLS (about 36 compounds listed in a table)
(-) all the phenolic compounds of the EC-list of priority pollutants (7 positions of the list = 9 compounds) with exeption of 2-amino-4-chlorophenol

TYPE OF SAMPLE

(-) all kinds of water samples, including ground water, surface water, effluents and sewage

RANGE OF APPLICATION

(-) determinations at concentrations above 0.1 ug/l possible (depending on the degree of enrichment; factors of 4000-10000 possible)

CALIBRATION

(-) various options:

(- -) calibration including or not including the total procedure
(- -) calibration with external standard or calibration with additional internal standard

STANDARD DEVIATION / RECOVERY

(-) data to be determined by intercomparison runs

IDENTIFICATION / CONFIRMATION

(-) Philosophy : gas chromatographic analysis with two capillary columns of different polarity

(-) in certain cases confirmation of the identification with selective detectors (like ECD or MS) recommended

Figure 19

PHENOLIC COMPOUNDS WHICH CAN BE ANALYZED WITH THE PROPOSAL FOR A STANDARD DIN 38 407 PART 10

Phenol
2-Methylphenol
3-Methylphenol
4-Methylphenol
2,4-Dimethylphenol
4-Ethylphenol
2,6-Di-tert.-butyl-4-methylphenol
2-Phenylphenol
2-Benzylphenol
4-Benzylphenol
2-Benzyl-4-methylphenol
2-Chlorophenol
3-Chlorophenol
4-Chlorophenol
4-Chlor-2-methylphenol
4-Chlor-3-methylphenol
6-Chlor-3-methylphenol
2,4-Dichloro-3,5-dimethylphenol
2,3-Dichlorophenol
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4,6-Trichlorophenol
2,3,5-Trichlorophenol
2,4,5-Trichlorophenol
2,3,6-Trichlorophenol
2-Nitrophenol
2,4-Dinitrophenol
2-Methyl-4,6-dinitrophenol
2,3,4,5-Tetrachlorophenol
2,3,4,6-Tetrachlorophenol
Pentachlorophenol
6-Chlorthymol
2-Chlor-4-tert.-butylphenol
4-Chlor-2-benzylphenol
2-Cyclopentyl-4-chlorophenol

horn4.rno

Figure 20

AROMATIC AND ALIPHATIC AMINES OF THE-EEC LIST OF PRIORITY POLLUTANTS

EEC-No.	COMPOUND	POSSIBLE WAY OF DETERMINATION BY :
2	2-Amino-4-chloro-phenol	HPLC
8	Benzidine	HPLC
17	2-Chloroaniline	HPLC
18	3-Chloroaniline	HPLC
19	4-Chloroaniline	HPLC
27	4-Chloro-2-nitroaniline	HPLC
41	2-Chloro-p-toluidine	HPLC
42	Chlorotoluidine (others than 2-Chloro-p-toluidine)	HPLC
52	Dichloroaniline	HPLC
56	Dichlorobenzidine	HPLC
72	Diethylamine	HPLC
74	Dimethylamine	HPLC

Figure 21

ORGANONITROGEN AND ORGANOPHOSPHOROUS PESTICIDES, AND PHENOXYLALKYL ACID HERBICIDES OF THE EEC-LIST OF PRIORITY POLLUTANTS

PART 1

EEC-No.	COMPOUND	POSSIBLE WAY OF DETERMINATION BY :
5	Azinphos-ethyl	HPLC
6	Azinphos-methyl	HPLC
45	2,4-D (including salts and esters)	HPLC
69	Dichlorprop	HPLC
80	Fenitrothion	HPLC
81	Fenthion	HPLC
88	Linuron	HPLC
90	MCPA	HPLC
91	Mecoprop	HPLC
95	Monolinuron	HPLC
107	2,4,5-T (including salts and esters)	HPLC

Figure 22

ORGANONITROGEN AND ORGANOPHOSPHOROUS-PESTICIDES, AND PHENOXYALKYL ACID HERBICIDES OF THE EEC-LIST OF PRIORITY POLLUTANTS

PART 2

(inclusive EEC-No. 114 :TRIBUTYLPHOSPHATE)

EEC-No.	COMPOUND	POSSIBLE WAY OF DETERMINATION BY :
43	COUMAPHOS	GC
44	CYANURCHLORIDE (2,4,6,-Trichloro-1,3,5-triazin)	GC
47	DEMETON (Iclusive Demeton-o,Demeton-s,Demeton-s-methyl, Demeton-s-methyl-sulphon)	GC
70	DICHLORVOS	GC
73	DIMETHOAT	GC-NFID
75	DISULFOTON	GC-NFID
80	FENITROTHION	GC
81	FENTHION	GC
89	MALATHION	GC-PFID
93	METHAMIDOPHOS	GC
94	MEVINPHOS	GC
97	OMETHOATE	GC
98	OXYDEMETON-METHYL	GC
103	PHOXIM	GC
104	PROPANIL	GC
105	PYRAZON	GC
106	SIMAZIN	GC
113	TRIAZOPHOS	GC
116	TRICHLORFON	GC
124	TRIFLURALIN	GC
114	TRIBUTYLPHOSPHATE	GC