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Instrumental Methods of Chemical Analysis

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The remarkable advances which have been made in the application of instruments to the problems confronting the chemist have been the topic of two previous communications in the ANALYTICAL EDITION (October, 1939 and 1940). In October, 1940, an initial treatment was concerned with a very general discussion of instruments of all kinds. It has become apparent that there is a real need for extensive, detailed discussions of various analytical methods. The editor has arranged for a series of expert reviews, several of which are in preparation. It seemed advisable to preface this series with some sort of preliminary survey or classification designed to illustrate the contemporary status of the field, to indicate the wide variety of techniques, and to dispel the notion, from which even the experts are not wholly immune, that progress is largely confined to a certain specialty or method. It is apparent that there is no "best" method for any kind of analysis.

The assignment of this problem to the author was based on no better recommendation than the last one—an interest in the subject and a pleasantly wide acquaintance with people who are doing important work in the field.

The collaboration which the author has had in this compilation is evident in the following pages. Several of the contributors of these examples are the experts whose detailed and authoritative expositions are to follow this review. Some serious defects and omissions are glaringly evident and the author's attempts to secure expert help and information were unsuccessful, in many cases for the reason satisfactory to every American—National Defense. This is no indication that those who could cooperate were not similarly committed and otherwise engaged in important and pressing work.

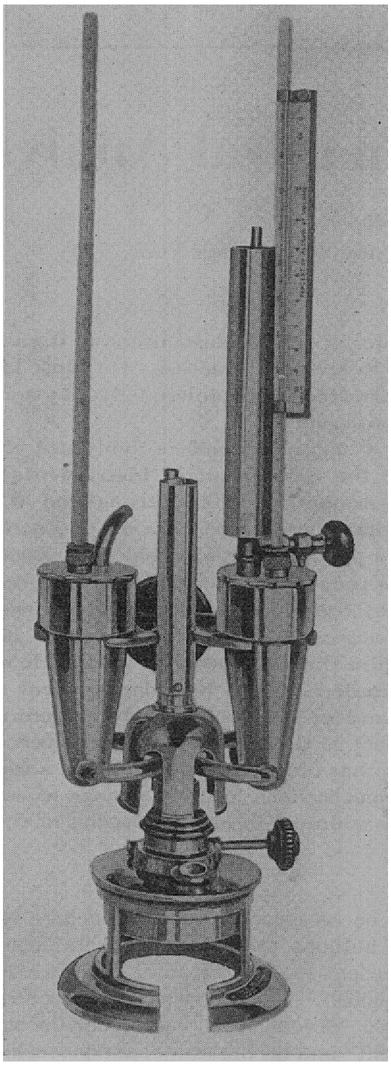
For the omissions and inaccuracies the author will plead the largeness of his design, with little hope for exoneration or clemency. The misplaced emphasis is intentional; in most cases the amount of discussion or detail is in inverse proportion to the state of development of the topic. Some instruments, which are fairly time-honored, are still treated in detail for reasons that are apparent. The literature dealing with some of the better known techniques is voluminous; in many it has become reduced to textbook practice. On those topics the few observations are opinionated and are not to be taken too seriously.

When a survey of modern analytical chemistry requires the description of instruments ranging from hydrometers to cyclotrons and it can be shown that these devices are all eminently practical and paying their way, one instinctively wonders how the modern analyst is to be appraised. It is evident from the contemporary scene that his former slogan "dry-ignite and weigh" no longer carries him through the day's work. He must become familiar with a bewildering array of techniques and at least moderately acquainted with the dialect of the physicist and engineer. By and large, he has done this and acquired a reputation for a broad outlook and wide range of experience none too common in other branches of chemistry.

IT WILL be necessary to explain the title of this review and the author's interpretation of its meaning. To be sure, a precedent exists (*165, 259*) for the use of "Instrumental Methods. . . ." but a special intent and purpose lie behind its use. Avoiding quibbles about the strict meaning of "instrument" and its Biblical, Shakespearean, and musical uses, it is generally considered to imply a tool, aid, adjunct, or means of accomplishing some purpose. These are too general for the author's purpose and he has tried to restrict the term to the interpretation preferred by instrument engineers. Although it has not been possible to adhere rigidly to the adopted definition in all cases, the concept may be illustrated by a specific example.

It is well known that the boiling point of a binary liquid mixture can be related to its composition either on the basis of theory or, if pronounced deviations from ideality exist, on an empirical basis. If the boiling point of an unknown sample were measured and appropriate corrections were made for the barometric pressure, the composition could be calculated from the standard boiling point–composition curve. This is a physical method of analysis based on a definite property of the system. The device shown in Figure 1 has extended this fundamental idea to the point where we may designate it as an instrumental method of analysis. In this case two liquids are boiling at the same time, the unknown liquid and pure water. When a steady state has been reached in the boiling process, the zero of a sliding scale on the thermometer which measures the boiling point of the unknown is set to the observed boiling point of the water thermometer. The position of the first thermometer is now read off from the adjacent scale which is calibrated not in degrees but in percentage composition (in the specific instance shown here per cent of alcohol by volume).

The improved technique has eliminated the need for barometric correction and the instrumental indication is in terms of the desired constituent. A physical method of analysis has been converted into an instrumental method of analysis.



Courtesy, C. J. Tagliabue Co.

Figure 1. Ebulliometer

Without intending to claim that we have hereby discovered a startlingly new principle, it does emphasize a point of view which has very important practical consequences. A rough analogy is to be found in the very common practice of calibrating volumetric solutions in terms of per cent of the desired constituent, even making due correction for a standard blank, instead of using the more formal scheme of normal or molar solutions. Although all devices are not conveniently designed to give a direct answer, it is to be regarded as the ultimate goal of a true instrument. In practice it boils down to the fact that in practical work computations must be reduced to a minimum, and although these may be the delight and pleasure of the research man the burden need not be tolerated if a comparable degree of ingenuity and skill can be exercised in the original design. In the following pages there are numerous examples, some of them time-honored, in which this ideal has been achieved; in others the need is so apparent that it at once explains the comparatively rare use made of the method despite its other attractive features.

If the intent of this term has been made clear it follows that many extremely important adjuncts to analysis cannot be considered here. That they are eminently worthy of discussion as important aids goes without saying. In addition, it will be found that we have not adhered consistently to our formulated definition of the instrumental method. Such methods are included nevertheless because by their nature they possess the inherent possibility of such development.

Density

Density is an unspecific property, but in systems of known composition it may be used as an accurate means of specifying concentrations (57). The simplest instrumental indication is afforded by hydrometers, and these devices are not only made to read specific gravity directly but may be obtained in a form which is calibrated directly to give the desired information. Typical examples are shown in Figure 2. Among some of the special scales we note alcohol, calibrated in per cent or in per cent of proof spirit; and scales to read calcium chloride, glue, salt, milk, sugar, sirup, or tanning liquor.

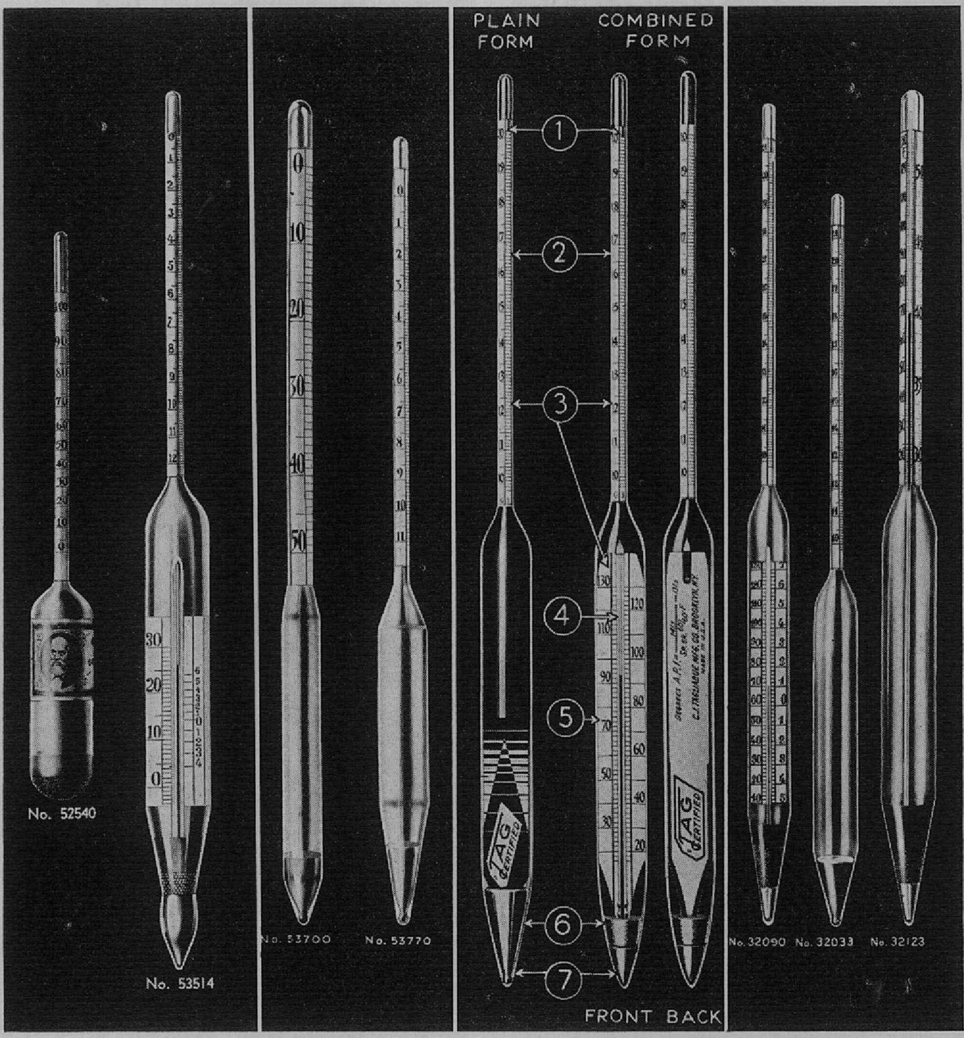
Precision hydrometers cover a restricted range and can be provided in a practical and technical form reading to one unit in the third place of specific gravity. This degree of precision translated into specific-purpose instruments might be illustrated by a precision sugar hydrometer covering a range of 69 to 81 per cent by weight which will give a reliable indication to 0.1 per cent. The proper use of hydrometers has been specified by the National Bureau of Standards and among other conditions assumes careful temperature control, equality of temperature of hydrometer and the liquid, and the use of the hydrometer with the liquid for which it is intended, because different surface tension effects may be revealed despite a common value of the density.

Specific Gravity Balance. The principle of the hydrometer may be extended with an increase of precision of about one order of magnitude by using a simple balance. Thus the Westphal balance (Figure 3) will read to about one unit in the fourth decimal place of specific gravity. This device becomes a means of a direct instrumental method of analysis if the scale is calibrated not in specific gravity units but in terms of the desired quantity.

Ultracentrifuge

A very long extrapolation from these simple devices is illustrated by the ultracentrifuge. This instrument is one of our most important means of studying substances of high molecular weight and is one of the few methods whereby information can be obtained from such complicated substances as proteins and polysaccharides. The specific sedimentation velocity is a constant characteristic of the dissolved unit, but it cannot be used without further information in calculating molecular weights on account of shape factors. Such information can be obtained, however, by a correlation between this quantity and diffusion constants.

Instruments and Methods. Two notable examples of this equipment are illustrated from the laboratories of well-known investigators in this field: Figure 4, the ultracentrifuge of the Svedberg type (270), with rotor cell and bearing housing, and Figure 5, the ultracentrifuge laboratory from the camera end of the instrument. The process of centrifugal sedimentation is followed by allowing light to pass through



Courtesy, C. J. Tagliabue Co.

FIGURE 2. SPECIAL-PURPOSE HYDROMETERS

windows in the rotor and photographing the position of the boundary between solvent and solution at stated intervals. Either the light absorption or the scale method (Lamm) may be used. Figure 6 shows an analytical ultracentrifuge for the study of plant and animal viruses and of the protein components of sera. This instrument is of the air-driven type (*18, 306*).

APPLICATIONS. Density methods have been widely used and in principle are well suited to the automatic recording and telemetering of information of analytical interest. Dozens of methods and uses of this type are described by Gmelin (*67*) and in engineering texts. The ultracentrifuge in conjunction with related techniques such as absorption spectra and electrophoresis has afforded information on the nature of high-molecular-weight compounds where ordinary analytical methods can give either no answer or at least only approximate information. The discussion of density has been limited here to liquids and solutions. It is more completely discussed in connection with gas analysis.

Thermal

Thermal methods include boiling point elevation and freezing point depression as well as the emission or absorption of heat accompanying chemical changes. These methods in general have limited analytical application but a few are

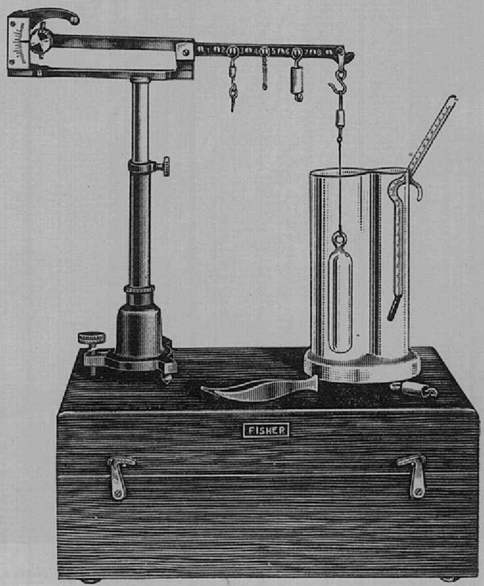


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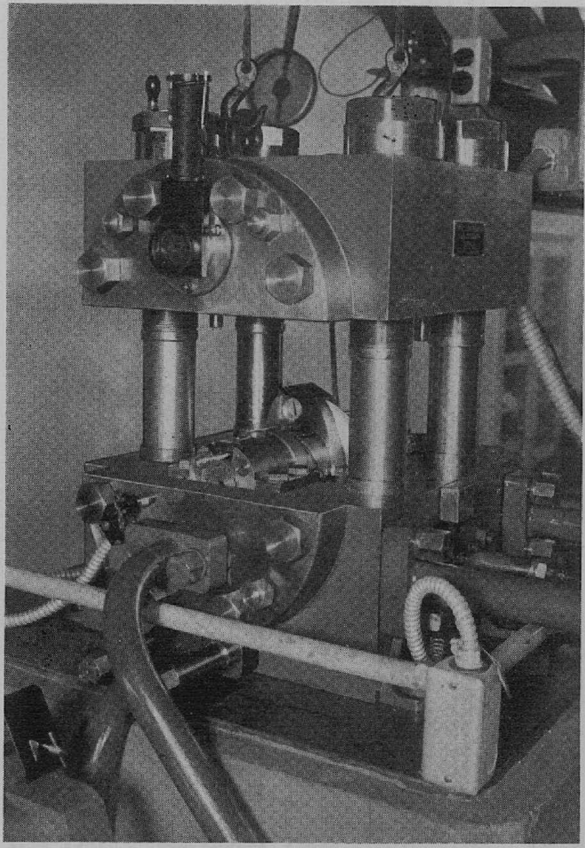
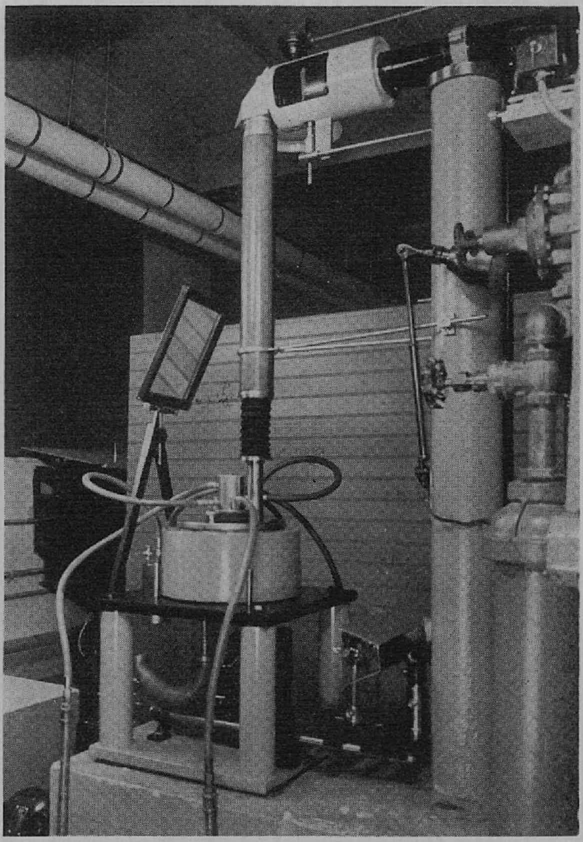
FIGURE 3. SPECIFIC GRAVITY BALANCE



Courtesy, J. W. Williams, University of Wisconsin

FIGURE 4. ULTRACENTRIFUGE, SHOWING CENTRIFUGE CASING, ROTOR, CELL, AND BEARING HOUSING



Courtesy, R. W. G. Wyckoff, Lederle Laboratories, Inc.

FIGURE 6. ANALYTICAL ULTRACENTRIFUGE

worthy of mention. The ebulliometer has been mentioned above. The freezing point depression for ideal solutions can be related simply to the composition, provided the molecular weight and the freezing point depression constant are known.

Courtesy, J. W. Williams, University of Wisconsin

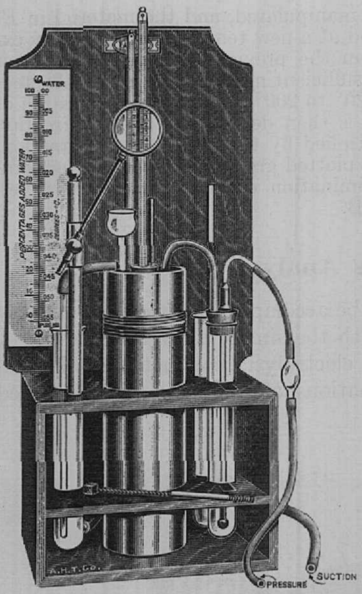
FIGURE 5. ULTRACENTRIFUGE LABORATORY, SHOWING CAMERA IN RIGHT FOREGROUND

The use of cooling curves in phase rule studies, particularly metallurgical, are well known and furnish information which is of importance in establishing the nature and composition of the various solid phases. The thermal techniques which are discussed under gas analysis might be included here.

INSTRUMENTS. Changes in temperature or the heat evolved in a process can be measured in a great variety of ways and are discussed in many standard works. We may mention in passing the use of gas and liquid thermometers, thermoelectric and resistance thermometry, and radiant heat by the thermopile and bolometer.

APPLICATIONS. A useful application of the freezing point method is illustrated in Figure 7, which shows the Hortvet cryoscope used for determining the amount of added water in milk. The freezing point is measured with a short-range thermometer graduated in 0.01° divisions. The freezing is accomplished by the evaporation of ether by a current of air, for which purpose a filter pump may be used. A scale attached to the instrument converts the observed temperatures directly to percentages of added water. The use of this instrument has been described in several places.

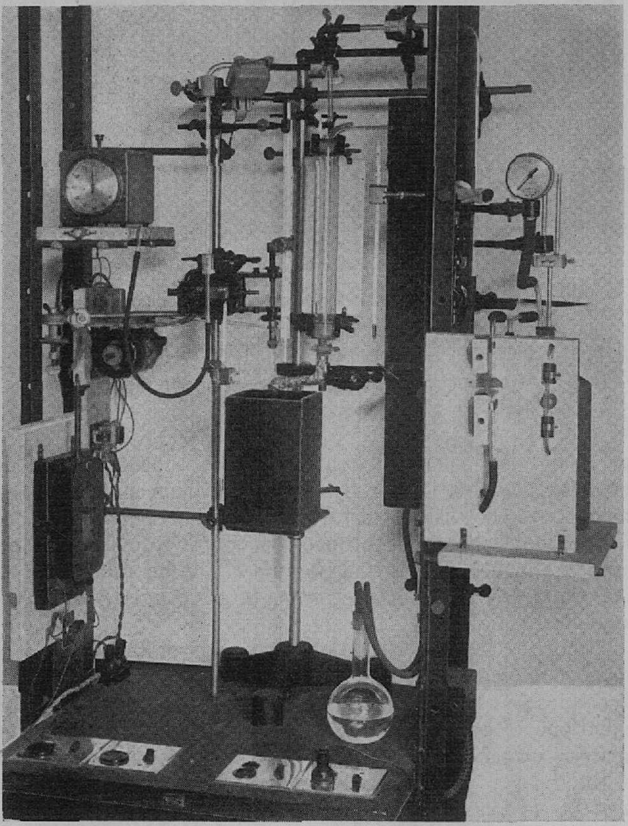
A measurement of the amount of heat evolved during the progress of a titration has been used on a number of occasions.



Courtesy, Arthur H. Thomas Co.

FIGURE 7. CRYOSCOPE

The first practical use seems to have been made by Bell and Cowell (*16*). Other examples have been described by Somiya (*264*). In general, the titration is carried out to within a few per cent of the end point and the change in temperature after small additions of reagent is noted. The measurements are continued somewhat beyond the end point and its true location is determined graphically. Most of the cases considered by Somiya were concerned with concentrated or fuming acids and the temperature rises were considerable. He points out, however, that the water content of concentrated sulfuric acid can be determined more accurately by thermometric titration than by acidimetry. With more refined measurements this technique can be extended profitably to much more dilute solutions.

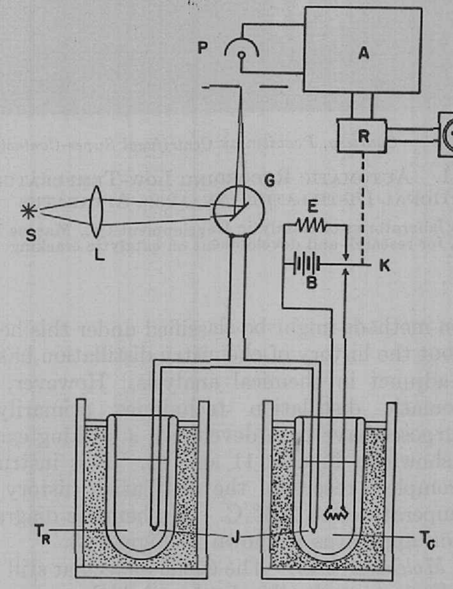


Courtesy, New York University

FIGURE 8. THERMOMETRIC TITRATION APPARATUS

Figure 8 shows an arrangement which has been used in the writer's laboratories for this purpose, with means for showing the titration both with the Beckman thermometer and by a differential thermoelectric method which is represented schematically in Figure 9. In the latter the heat evolution in the titration vessel is exactly and automatically compensated by the electrical addition of heat in the reference vessel. The multijunction thermocouple and galvanometer control this process through the agency of a simple photoelectric relay which switches a constant heating current on or off. A Telechron clock indicates the time during which constant heat is imparted to the reference cell. The elapsed time is therefore proportional to the heat which has been evolved as a result of the titration increment (Figure 10).

These methods are not particularly useful unless considerable heat is evolved or unless automatic means such as the one described are used to measure the temperature rises. Unless the results are automatically recorded and evaluated, the need for graphic computation of the end point has the same time-consuming drawback characteristic of other methods such as conductance titrations.



Courtesy, New York University

FIGURE 9. THERMOMETRIC TITRATION APPARATUS

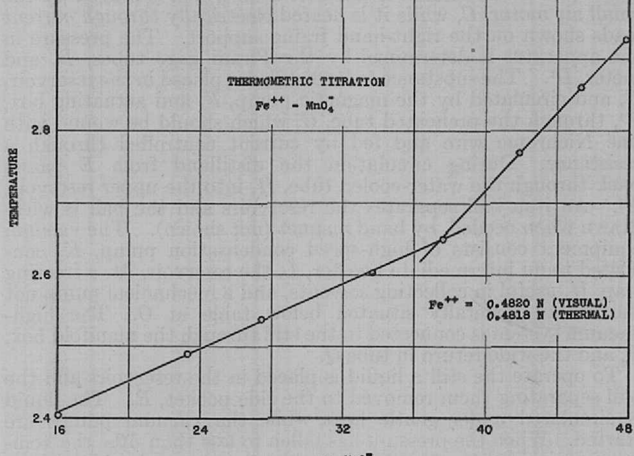


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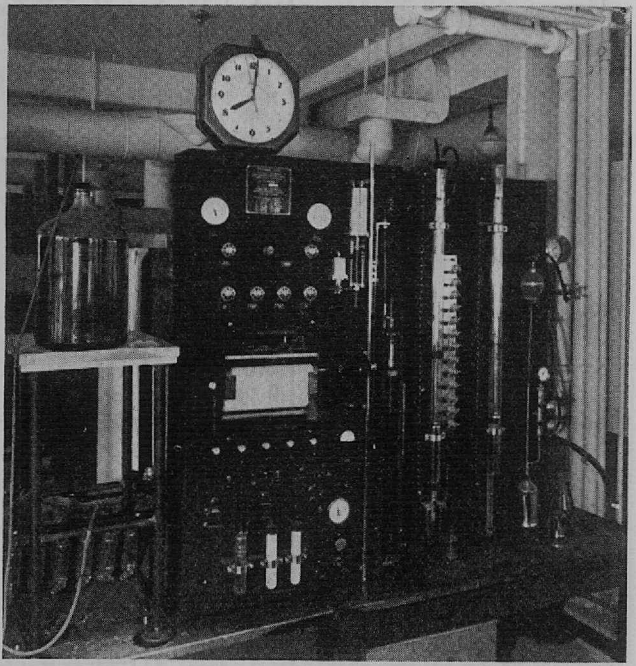
FIGURE 10. THERMOMETRIC TITRATION CURVE



Courtesy, Podbielniak Centrifugal Super-Contactor Co.

FIGURE 11. AUTOMATIC RECORDING LOW-TEMPERATURE FRACTIONAL DISTILLATION ANALYSIS APPARATUS

Installation in laboratories of Catalytic Development Co., Marcus Hook, Penna., for research and development on catalytic cracking

Distillation methods might be classified under this heading and throughout the history of chemistry distillation has been used as an adjunct in chemical analysis. However, completely automatic distillation techniques primarily for analytical purposes have been developed, a striking example of which is shown in Figures 11 and 12. This instrument provides a complete record of the distillation history from liquid air temperatures to 250° C. A schematic diagram of the distillation apparatus is shown in Figure 13.

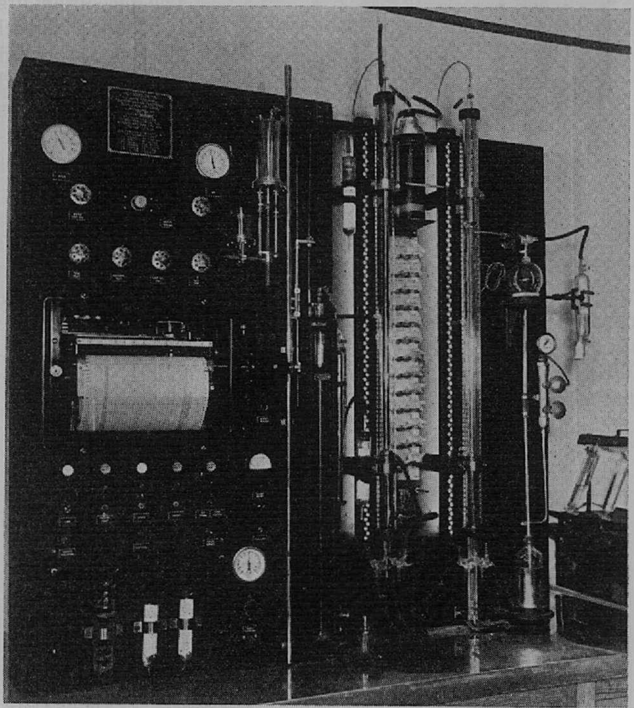
Analytical Molecular Still. The cyclic molecular still is the outcome of efforts to make the short-path high-vacuum surface evaporator into a tool for exact analysis and research. The apparatus in its present stage of development is shown in Figure 13A.

A is the distillation column contained within the glass condenser, B. The column is filled with oil which is stirred by the small air motor, C, while it is heated electrically through current leads shown on the right-hand frame support. The pressure in the apparatus is determined by the Pirani gage tubes, D, and meter, D^1. The substance to be distilled is placed in the reservoir, E, and circulated by the magnetic pump, F, and actuating box, F^1, through the preheated tube, G, which should be wound with fine Nichrome wire and fed by current controlled through a resistance. During circulation the distilland from E passes back through the water-cooled tube, H, into the upper reservoir, E^1. An iron ball separates the reservoirs and the ball is withdrawn when needed, by hand magnet (not shown). The vacuum equipment consists of high-speed condensation pump, K, connected to an intermediate booster, L, the reservoir, M, a freezing trap, N, useful in collecting solvents, and a mechanical pump not shown but generally situated below table at O. The high-vacuum system is connected to the still through the manifold box, P, and the wide return in tube Q.

To operate the still a liquid is placed in the reservoirs and the ball separating them removed to the side pocket, R. The liquid is circulated under gentle heat while the vacuum pumps are started. When the pressure has fallen to less than 10μ the temperature is fixed at a predetermined level and samples of the fraction are collected in the receiver, S. After one complete cycle (the ball having been placed in position at the beginning of the cycle) the stopcock, T, is manipulated, receiver S changed to a new one, stopcock T again manipulated, and the material in E^1 let down to E and circulated at a new temperature generally exactly 5° or 10° higher than the previous one. This series of operations is kept up until sufficient material has been collected, generally over a range of 120° to 200° C. The concentration of all constituents of interest is then determined in each fraction and the concentration multiplied by the weight of the fraction, which equals total yield, is plotted graphically against temperature. There results an elimination curve or series of curves, such as shown in Figure 13B.

Gas Analysis

The analysis of gas can be accomplished by a great variety of techniques, starting with the simple absorption methods, bell chamber equipment, electrolytic conductance, thermal conductance, and combinations of these methods preceded by preliminary chemical treatment, by the heat evolved in catalytic combination, or by optical methods, including absorption in the visible, ultraviolet, and infrared, as well as refractometric methods utilizing the interferometer. They range from the analysis of a fraction of a cubic millimeter to the completely automatic recording of gas composition on an industrial scale (*54*).



Courtesy, Podbielniak Centrifugal Super-Contactor Co.

FIGURE 12. AUTOMATIC RECORDING LOW-TEMPERATURE FRACTIONAL DISTILLATION ANALYSIS APPARATUS

Installation in laboratories of Lion Oil Refining Co., El Dorado, Ark., for analysis of natural gas and gasolines and for separate determination of paraffin and olefin in C_3 and C_4 cracked refinery gas fractions

THEORY. Our knowledge of the gaseous state is in a high state of development and the contributions from thermodynamics and the kinetic theory have provided very accurate equations of state. Several of the methods used for the analysis of gas are based upon straightforward applications of the theory. Others, such as thermal conductance and the heat of catalytic conversion, for the most part require empirical calibration; for, despite extensive theoretical investigations, the predictions of the properties of mixtures, especially in the case of thermal conductance, are not accurate enough for analytical purposes. The wide range of applicability and the extreme sensitivity of some of the instrumental methods make this one of the most important branches of analytical chemistry.

INSTRUMENTS AND METHODS. *Determination of Gas Density.* The measurement of gas density is extremely important and has formed the basis for many automatically recording systems. The gas density balance illustrated in Figure 14 is based on a measurement of the pressure of the gas necessary to bring a balanced float to a standard equilibrium position under conditions of constant temperature. Its uses have been described by Edwards (*62*). It is applicable to a wide range of systems, but since density is an unspecific property, in some cases the measurement must be preceded by chemical treatment. Numerous recording methods for engineering applications have been described (*71*). In one method the streaming gas properly throttled flows into one tube and displaces a suitable manometric liquid into another limb of the tube (*278*).

Among the dynamic methods the effusion velocity principle has been applied in a number of ways by allowing the gas to diffuse out through a pinhole orifice (*65*). The density and composition of simple mixtures can be inferred from the rate of effusion. Here, too, theoretical predictions are not too helpful because the mixture laws apply only with systems containing molecules with the same number of atoms and viscosity coefficients that do not differ too widely. As a rule empirical calibration is necessary. An example of this type of instrument is shown in Figure 15.

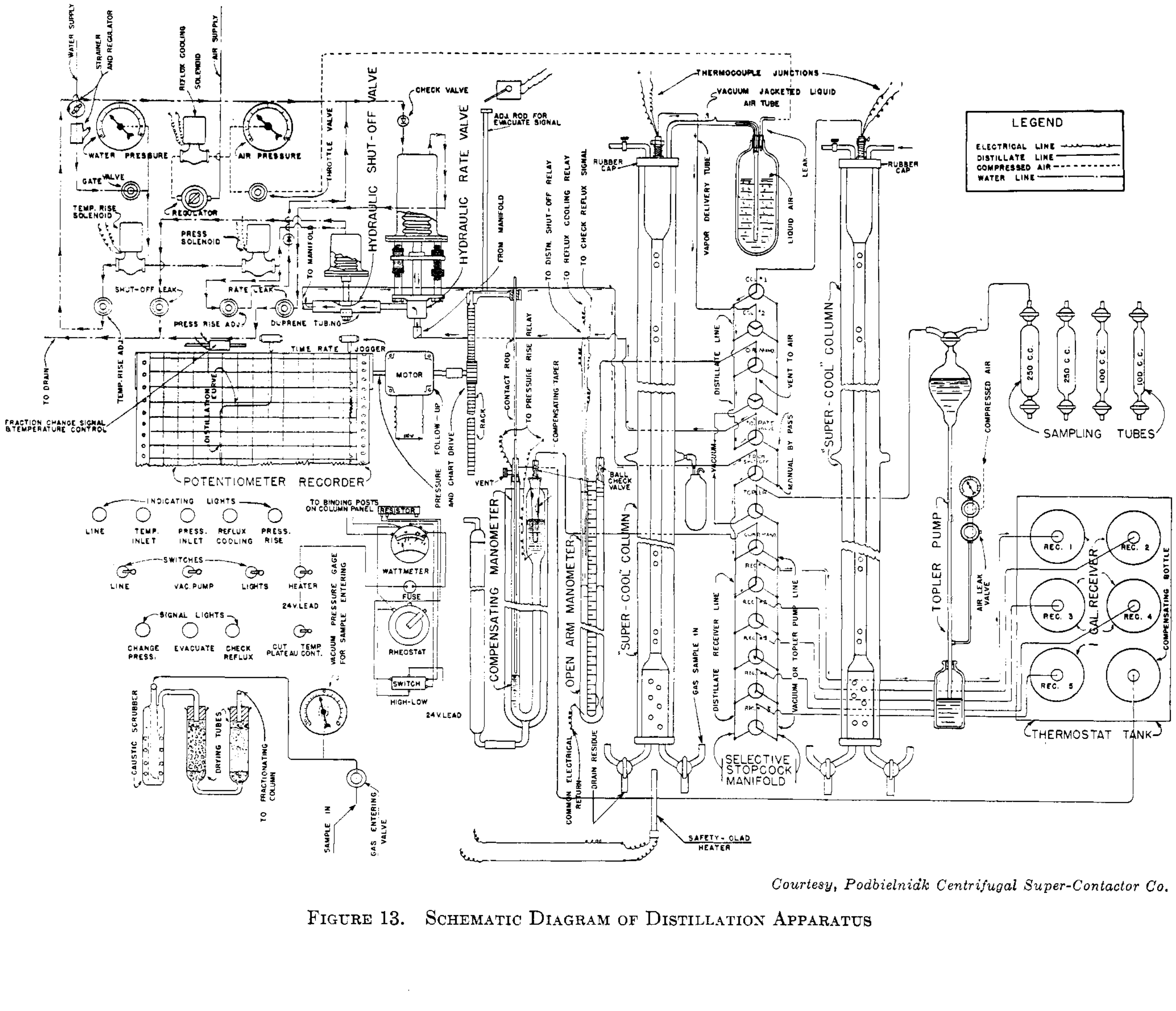
Effusiometers of the recording type employ a diving bell principle or floating plunger to actuate the recording pen. These arrangements are well suited for telemetering.

The Ranarex principle depends upon an aerodynamic coupling between a motor-driven ventilator fan and a similar fan which is connected with the indicating mechanism. The degree of coupling is a function of the gas density (Figure 16).

The many extensions and elaborations of these principles have been described (*57, 65, 71, 260,* and in standard engineering works).

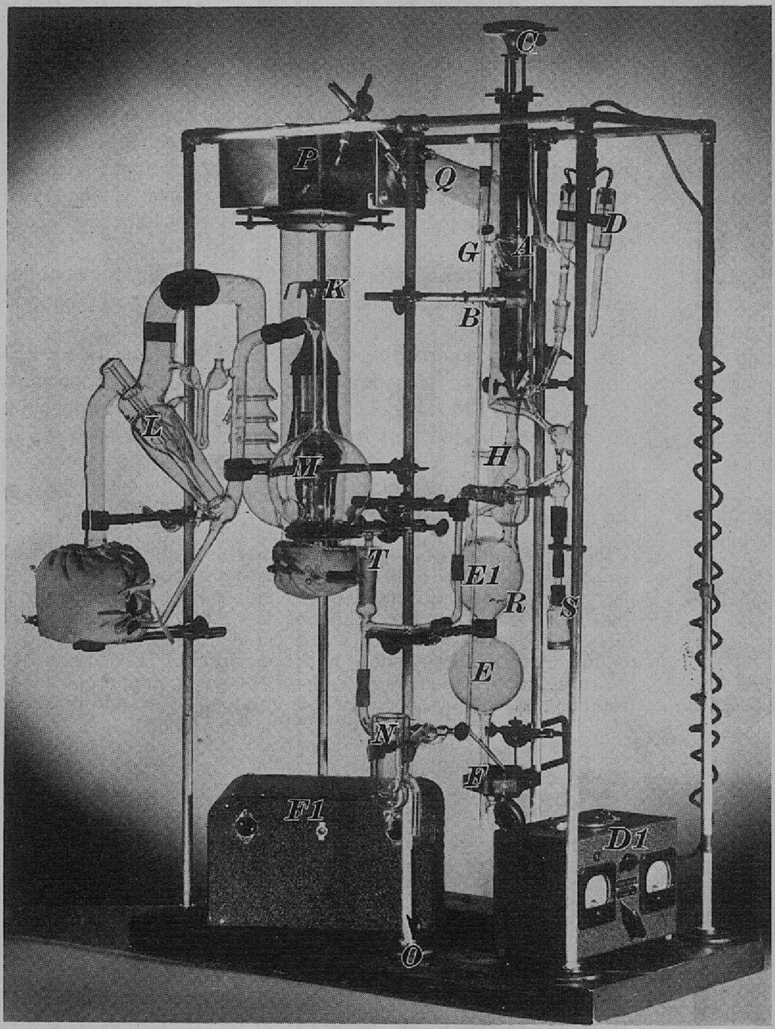
ABSORPTION TECHNIQUES. The classical absorption techniques form the subject matter of many treatises and manuals (*65, 69, 92, 93, 115, 181, 212, 297, 301*). A typical example of a modern coordinated unit for the analysis of gases is shown in Figure 17. Very frequently a problem reduces to detection of a gas and a rough quantitative indication, particularly in the case of highly toxic or otherwise hazardous gases.

Figure 18 indicates a convenient portable hydrogen sulfide detector. The simple bulb aspirator draws a sample of the suspected air through a renewable detector tube. The reaction of hydrogen sulfide on the filling of the tube produces a color change, the extent of which is compared with an adjacent scale reading directly in per cent of hydrogen sulfide. The instrument indicates the actual concentration of the gas in amounts ranging from 0.0025 to 0.04 per cent by volume. The calibration is



Courtesy, Podbielnidk Centrifugal Super-Contactor Co.

FIGURE 13. SCHEMATIC DIAGRAM OF DISTILLATION APPARATUS



Courtesy, Distillation Products, Inc.

FIGURE 13A. MOLECULAR STILL

based on the assumption that the bulb has been squeezed ten times, expanding completely after each aspiration. Figure 19 illustrates the convenient portable nature of the equipment for field work and the simple renewal with reagent cartridges.

One of the nicest examples of refinements in the general technique is to be found in the modern means for analyzing extremely small amounts of gas. Of these the systematic developments and studies by Blacet and Leighton (*19–23*) form an outstanding example. The apparatus which they have developed for this purpose is shown in Figures 20, 21, and 22. The merit of their equipment lies not merely in the small samples which can be accommodated but more particularly in the high degree of selectivity and precision. This is best illustrated by an excerpt from one of their papers (*22*) as shown in Table I.

TABLE I. ANALYSES FOR ACETYLENE IN THE PRESENCE OF PROPYLENE AND CARBON MONOXIDE

Determination	Volume of Sample	Theoretical	Acetylene Determined	Difference
	Cu. mm.	%	%	%
1	45.44	33.10	33.09	−0.01
2	40.75	33.10	32.98	−0.12
3	37.66	33.10	33.15	+0.05
4	40.82	33.10	33.11	+0.01
5	42.61	33.10	32.80	−0.30
			Av. 33.03	0.10

Another approach to the microanalysis of gases is to be found in the early work of Langmuir in analyses conducted at very low pressures. These are discussed in great detail in several monographs on high-vacuum technique (*60, 97, 206*).

Another approach to the microanalysis of gases is to be found in the Barcroft-Warburg manometer, which has widespread use in biological investigations. This equipment, examples of which are shown in Figures 23 and 24, is useful not only in measuring small amounts of gas but in following the kinetics of gas reactions. Some applications of the equipment, illustrated in Figure 23, have been described (*9, 146*).

Bell Chamber Methods. The general principle involved in this technique consists in trapping the gas under a floating bell in which the supporting liquid contains a reagent that absorbs the gas. Thus in the specific instance of a recording carbon dioxide meter the liquid is a concentrated solution of sodium hydroxide. As the carbon dioxide in the gas is absorbed the diving bell sinks and moves the indicating or recording element in proportion to its motion. This instrument is exemplified by numerous combustion recorders and in the medical field by metabolism apparatus (Figure 25).

This class of instrument is also suited to telemetering, in which case the moving element upsets the balance of an inductive bridge, or through related transfer mechanisms (*71*).

Electrical Conductivity. This technique is more properly discussed under electrolytic conductance, but instruments of this class are based on the absorption of the gas in question by a suitable electrolyte, after which changes in the conductance of the solution are measured. It has been used specifically for the measurement of water vapor, carbon dioxide

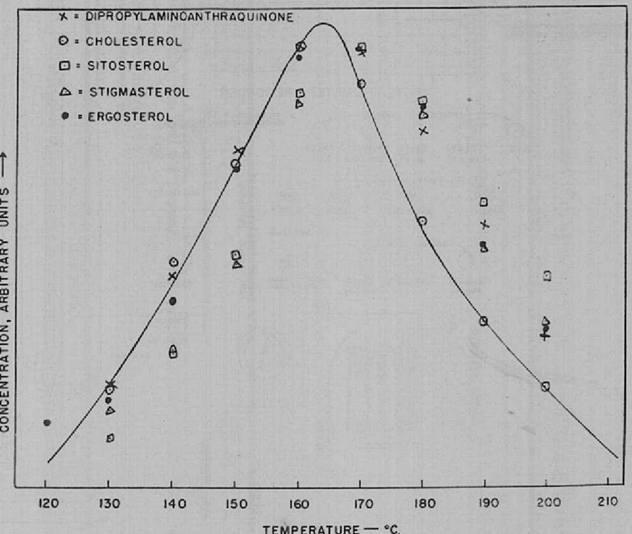


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FIGURE 13B. ELIMINATION CURVE FOR MOLECULAR STILL

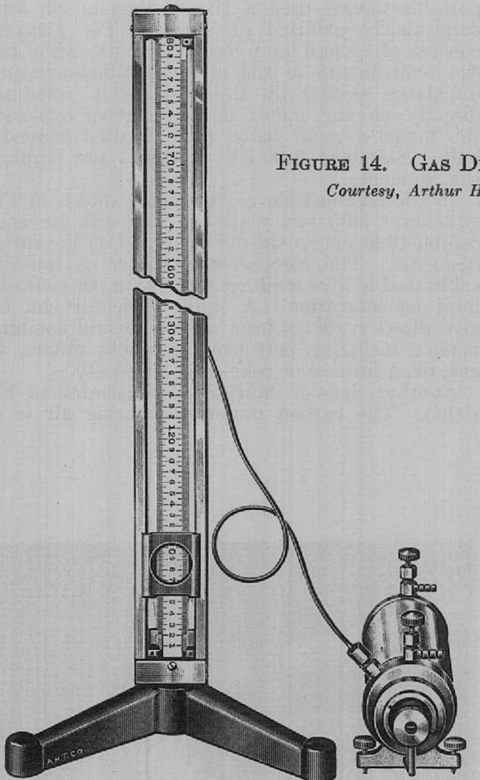
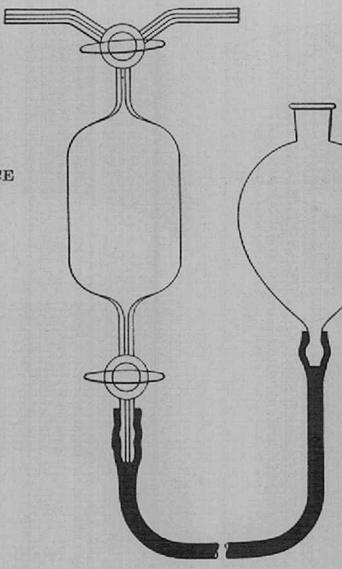
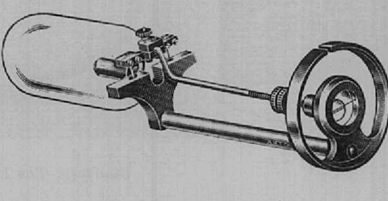
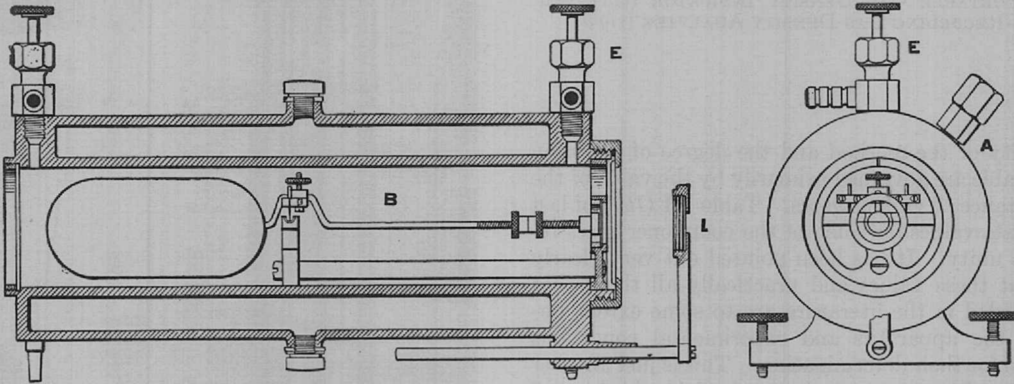


FIGURE 14. GAS DENSITY BALANCE
Courtesy, Arthur H. Thomas Co.





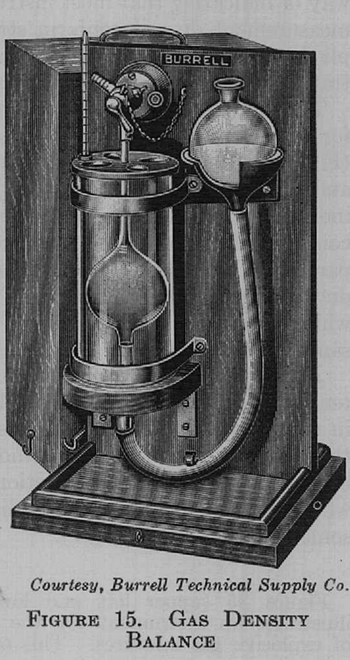


(*291, 300*), and sulfur dioxide, although in principle any gas which can be made to react with a suitable electrolyte may be used—i. e., carbon monoxide has been analyzed by this method by preliminary catalytic conversion to carbon dioxide, which is measured in the ordinary way. Equipment of this sort has been used to measure carbon dioxide in the conventional combustion train. Instrumental details are described in most treatises on conductometric analysis.

Thermal Conductance. This very important method of gas analysis is based on the thermal conductivity of the gas as a function of its composition. At atmospheric pressure the thermal conductance is relatively independent of the pressure and solely a function of the composition of the gas. At low pressures (10^{-2} to 10^{-5}) the thermal conductivity of a gas in a given cell is extremely sensitive to pressure and indeed forms the basis of a very sensitive pressure gage (Pirani gage).

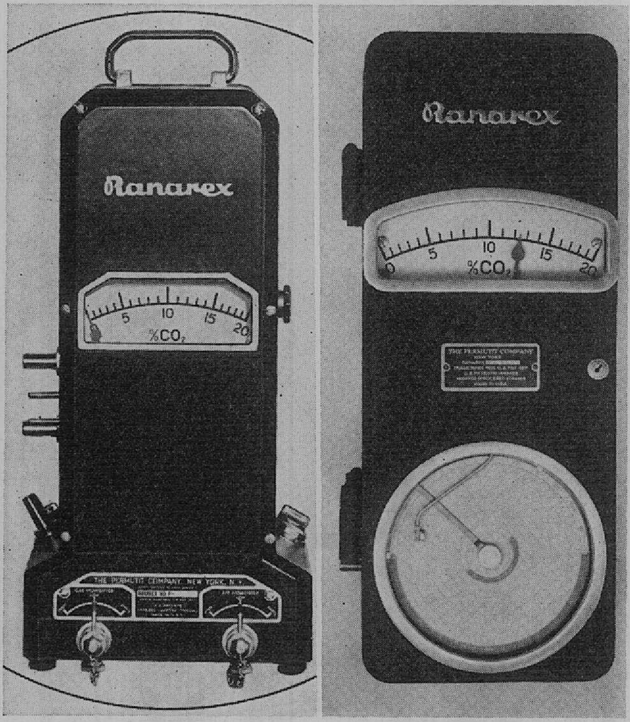
The simplest thermal conductance gage consists of two contiguous chambers. Along the axis of each chamber is stretched a fine wire having a high-temperature coefficient of resistance, usually platinum. The wires form two arms of a Wheatstone bridge. One wire is surrounded by a standard reference gas and the other by the gas to be analyzed. The two wires are heated by the bridge current to a temperature of the order of 100° C. above the surrounding and the heat loss by gas conduction determines the effect of temperature of the wire, which in turn determines its electrical resistance and therefore the state of balance of the bridge.

The complete theory and practice of this principle have been described in many places and are the subject of an excellent monograph (*51*), which gives complete details of the underlying theory and the characteristics and particular advantages of the various bridge circuits.



Courtesy, Burrell Technical Supply Co.

FIGURE 15. GAS DENSITY BALANCE



Courtesy, The Permutit Co.

FIGURE 16. PORTABLE GAS DENSITY INDICATOR (*left*) AND INDICATING-RECORDING GAS DENSITY ANALYZER (*right*)

The suitability of the method and the degree of precision which is obtainable are governed primarily by the value of the specific conductance of various gases. Table III (*197*) of last year's review lists values for some of the commoner gases referred to air as unity. It has been pointed out very clearly by Daynes that these values and practically all those that have been recorded in the literature are to some extent dependent upon the apparatus and experimental conditions which were used for their determination. This is just another way of indicating that most instruments used for this kind of measurement do not conform strictly to the conditions implied in the definition of thermal conductance. It also illustrates why empirical calibration is necessary.

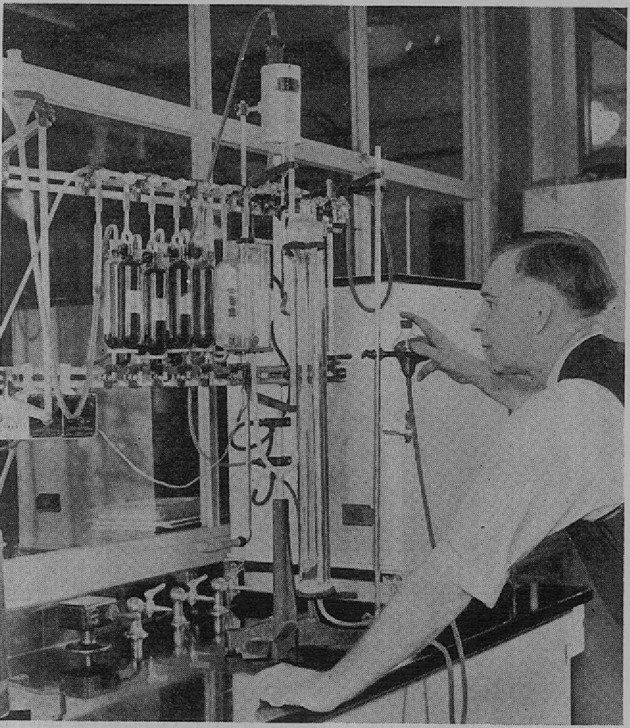
The many applications of this principle include equipment for the automatic analysis of dissolved oxygen in feed water (Figures 26 and 27), of carbon dioxide (Figures 28 to 31), and of sulfur dioxide (Figure 32). Perhaps one of the best indications of the wide range of utility is shown by the comparative records of Figure 33. Of particular interest is the trend toward the development of all-glass cells (Figure 34) which permit the use of relatively corrosive samples (*106*, *226*, *293*).

Heat of Catalytic Conversion. An extension of thermal methods which at least in some instrumental aspects is similar to the thermal conductance method is the utilization of the heat of reaction evolved when the gas in question is subjected to some chemical reaction (*81*).

Figure 35 (upper left and lower right) illustrates an instrument for the detection of explosive gas mixtures. This completely portable device uses a single filament on which the gas is catalytically oxidized or burned. The compensating resistor consists of a small lamp bulb. The process of combustion raises the temperature of the measuring filament and the electrical unbalance caused by the increase in resistance is indicated directly on the meter in per cent of explosive mixture. In this model a small piston pump is used instead of an aspirator bulb. Standard flashlight batteries are employed for heating the filaments.

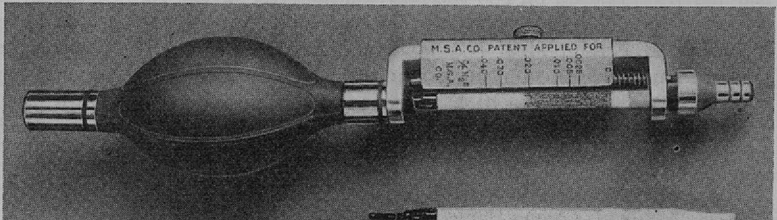
In the combustible gas indicator shown in Figure 35 (center and lower left) two platinum filaments are employed and the combustible gas is oxidized or burned on the surface of one of the filaments. The electrical unbalance is indicated on a scale calibrated to give readings directly in per cent of lower explosion limit concentration. A single indicator can be calibrated to give direct readings from one or several combustible gases and vapors, including petroleum, alcohols, ethers, acetone, natural gas, blast furnace or coke-oven gases, etc.

Another class of indicator is illustrated in Figure 35 (upper right). The carbon monoxide-bearing air is drawn into the



Courtesy, Burrell Technical Supply Co. and Buick Metallurgical Dept., General Motors Corp.

FIGURE 17. USE OF GAS ANALYSIS APPARATUS IN METALLURGICAL LABORATORY



Courtesy, Mine Safety Appliances Co.

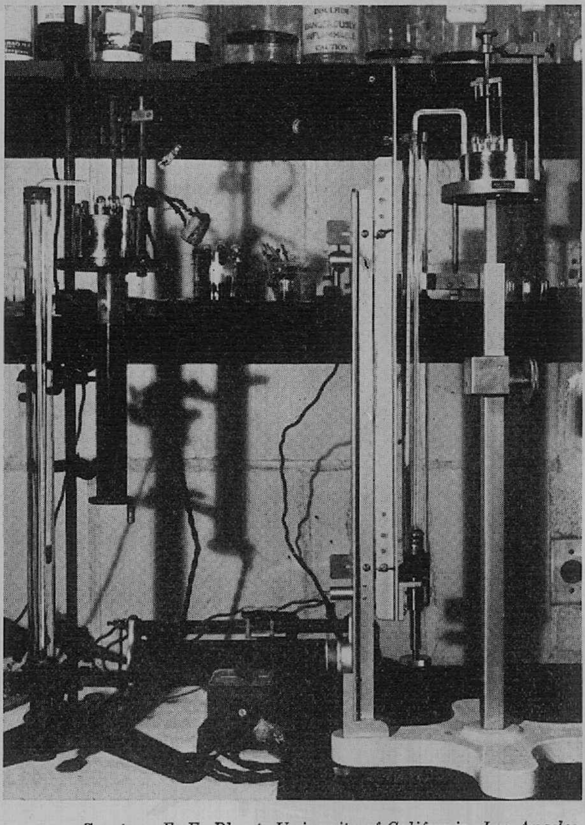
FIGURE 18. HYDROGEN SULFIDE DETECTOR

A hand-operated instrument for quick and accurate detection and measurement of low but dangerous concentrations of hydrogen sulfide.

Courtesy, Mine Safety Appliances Co.

FIGURE 19. HYDROGEN SULFIDE DETECTOR

* * *

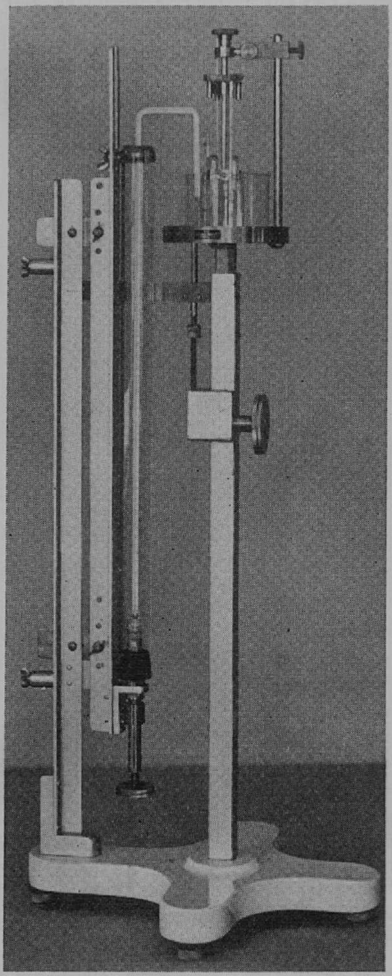


Courtesy, F. E. Blacet, University of California, Los Angeles

FIGURE 20. TWO FORMS OF BLACET-LEIGHTON APPARATUS FOR MICROANALYSIS OF GASES

(*Left*) Eimer & Amend style
(*Right*) Arthur H. Thomas Co. style

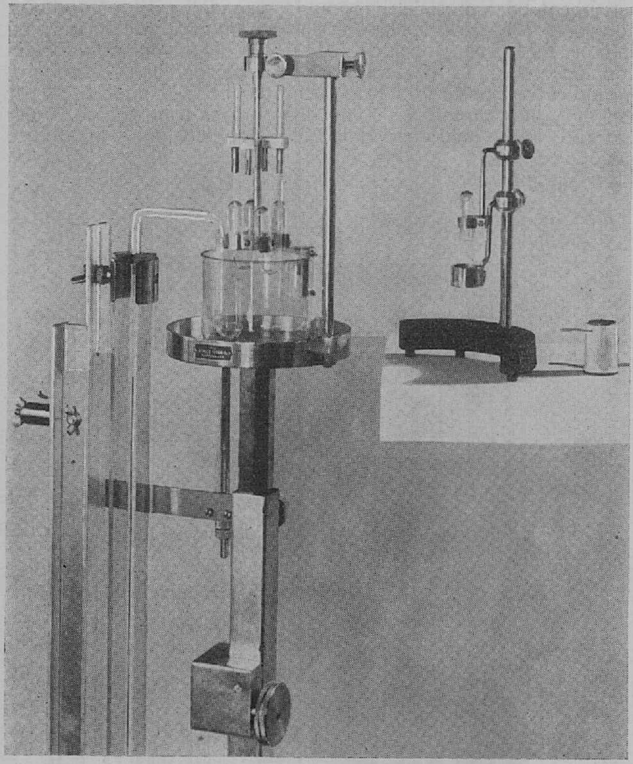
instrument by a motor-driven pump provided with a flowmeter indicator. The gas is drawn through a catalytic conversion chamber filled with Hopcalite. The heat of conversion to carbon dioxide is measured by the series of thermocouples in series with the indicating meter which is calibrated to read directly in per cent of carbon monoxide. The scale ranges from 0 to 0.15 per cent and can be read directly to 0.005 per cent and estimated to 0.001 per cent. In a hand-driven model a small highly efficient four-cylinder radial pump develops proper suction for sampling and an automatic regulator maintains the correct sample flow which is indicated on a diaphragm-type pressure gage. The motor-driven type could be operated from any 6-volt alternating or direct current supply or from self-contained Edison storage batteries.



Courtesy, Arthur H. Thomas Co.

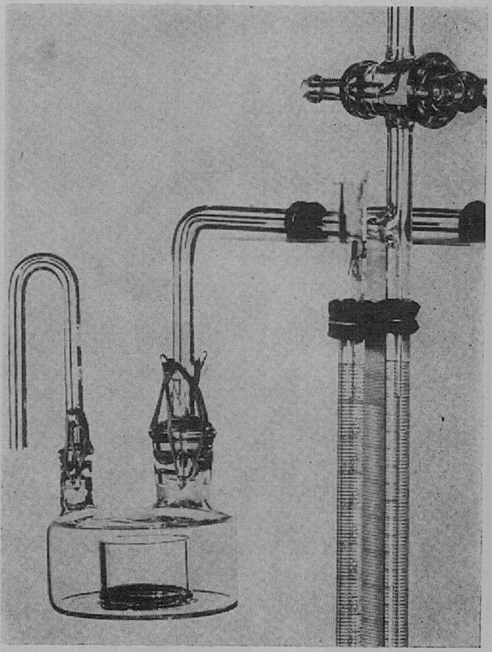
FIGURE 21. BLACET-LEIGHTON GAS ANALYSIS APPARATUS

Two extensions of this principle, shown in Figures 36 and 37, provide automatic alarm features. The one shown in Figure 36 contains a ventilating fan delivering 20 liters of air per minute. The sample passes through a divided cell containing active and inactive Hopcalite. Thermocouples indicate the differences in temperature of the two cells on a scale which is calibrated directly in per cent of carbon monoxide. If the carbon monoxide exceeds 0.02 per cent the meter closes a circuit and sounds an alarm which persists until the meter is manually reset. The model shown in Figure 37 is a completely explosion-proof combustible gas alarm that contains two platinum filaments in a balanced circuit. Catalytic combustion on one of the filaments with a consequent



Courtesy, Arthur H. Thomas Co.

FIGURE 22. DETAILS OF BLACET-LEIGHTON GAS ANALYSIS APPARATUS

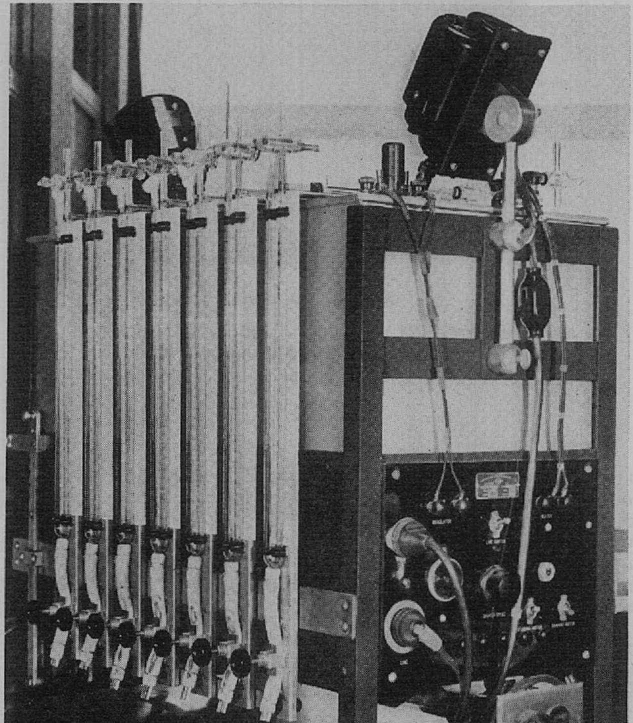


Courtesy, C. N. Frey, Fleischmann Laboratories, Standard Brands, Inc.

FIGURE 24. FLASK-MANOMETER ASSEMBLY FOR BARCROFT-WARBURG APPARATUS

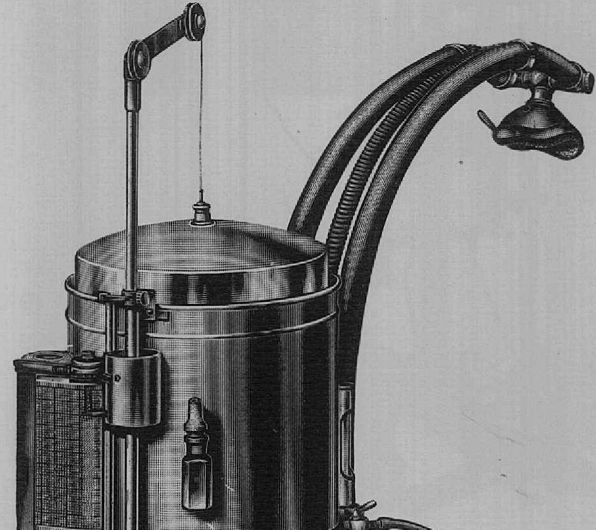
temperature rise unbalances the circuit and indicates directly on the scale calibrated for the gas in question. When the meter reading exceeds a predetermined limit an alarm is sounded which persists until the circuit is manually restored. A nonsparking diaphragm pump furnishes the circulation of the gas.

A very complete classification of the characteristics and applicability of the catalytic conversion technique (*71*) gives details concerning the nature of the gas, range of concentrations, temperature effect per unit per cent of the gas-measuring element, sensitivity, appropriate catalyst, and the field of



Courtesy, C. N. Frey, Fleischmann Laboratories, Standard Brands, Inc.

FIGURE 23. BARCROFT-WARBURG APPARATUS



Courtesy, Fisher Scientific Co.

FIGURE 25. METABOLISM APPARATUS

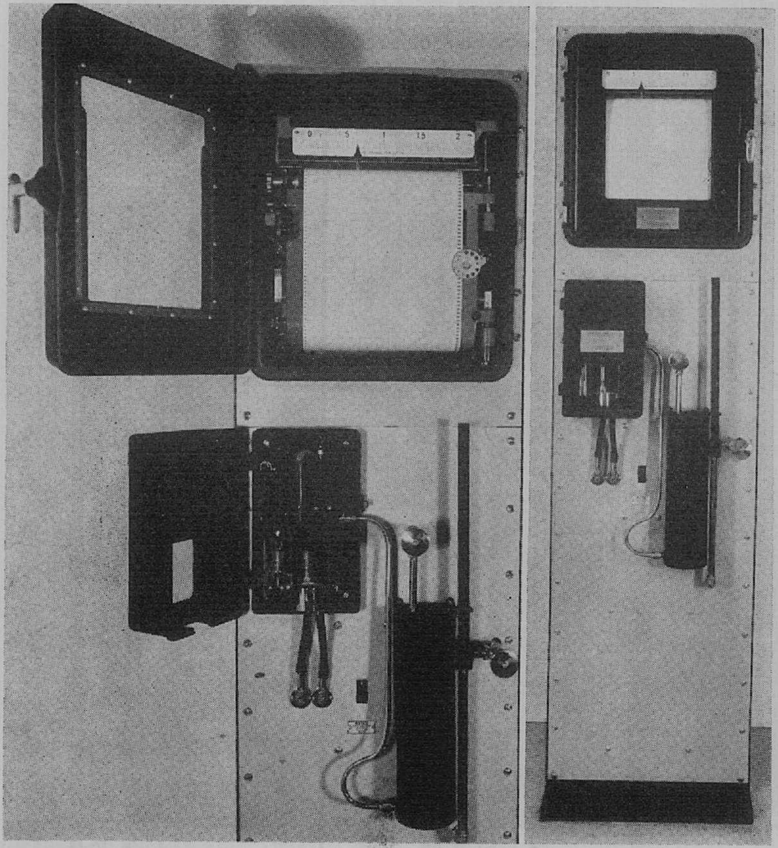


FIGURE 26. DISSOLVED OXYGEN ANALYZER

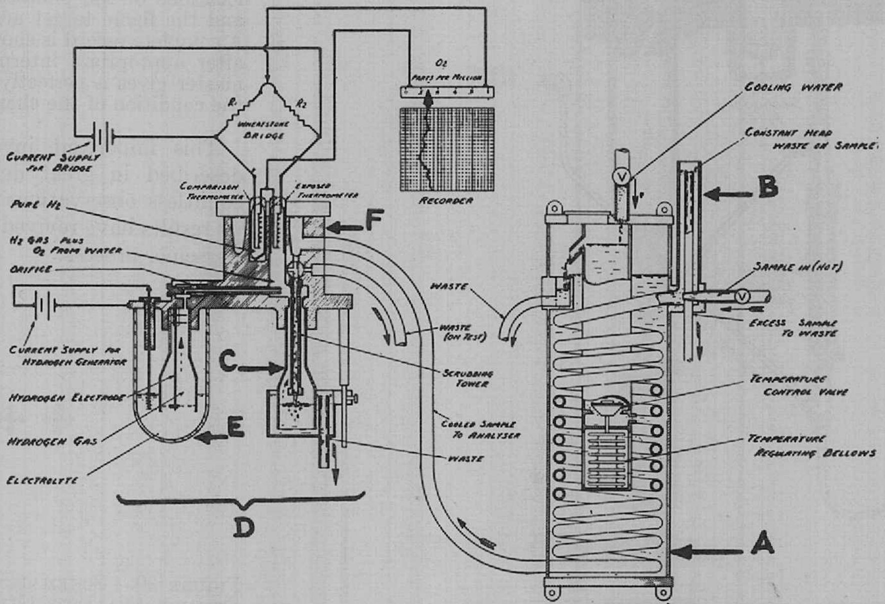
Courtesy, Cambridge Instrument Co., Inc.

application. In addition to the gases already discussed, ammonia, hydrogen sulfide, methane, hydrogen, and the vapors of benzene and alcohol are included. This list is concerned with actual installations and in principle any system which can be subjected to preliminary chemical treatment can be followed by one of the foregoing instrumental methods.

⁂

Optical Methods. Any of the methods discussed below in connection with optical instruments can be applied to the detection or analysis of gases, and this applies for the visible, ultraviolet, and infrared regions of the spectrum. Chlorine, bromine, or iodine vapor is amenable to photometry in the visible, mercury vapor and many hydrocarbons can be detected in vanishingly small amounts in the ultraviolet, and carbon dioxide to the extent of less than 0.0001 per cent can be detected by a characteristic absorption band in the infrared. The use of the interferometer (*63*, *64*) for very exact analyses of gases is discussed in connection with refractive index.

CONCLUSION. The general topic of gas analysis covers an extremely wide range of techniques and particularly from the industrial point of view is in a high state of development. Some of the indirect applications of these methods are startling and in some cases have revived old and almost discarded practices. One illustration which bears this out is difficult to classify but may truly be characterized as an optical method for the analysis of incandescent gas or vapor.



Courtesy, Cambridge Instrument Co., Inc.

FIGURE 27. SCHEMATIC DIAGRAM OF DISSOLVED OXYGEN RECORDER

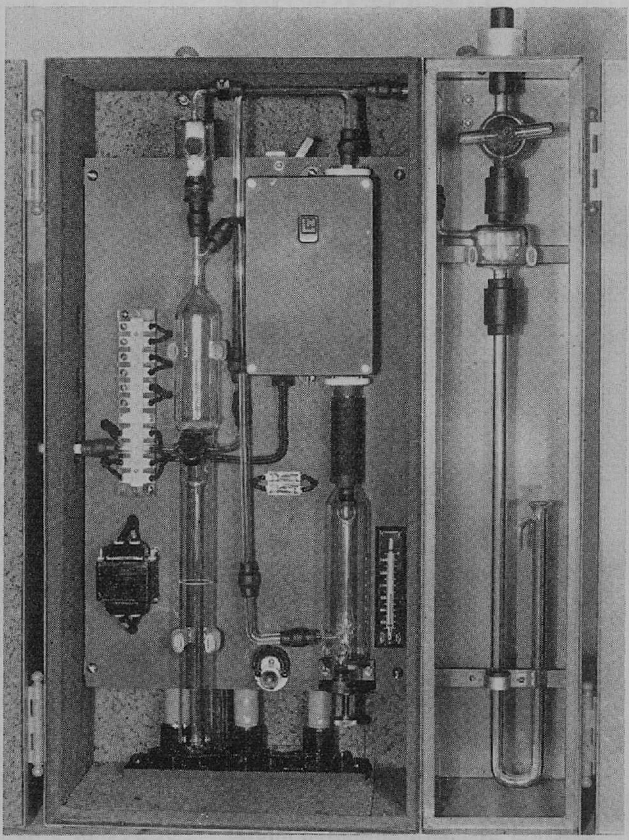
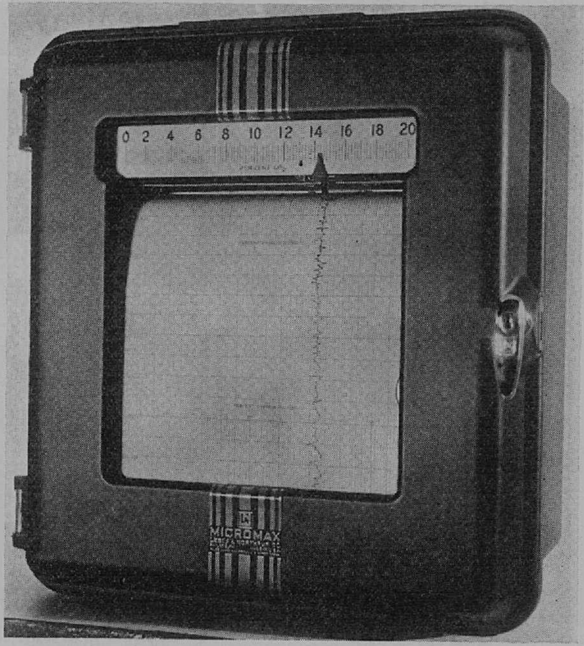


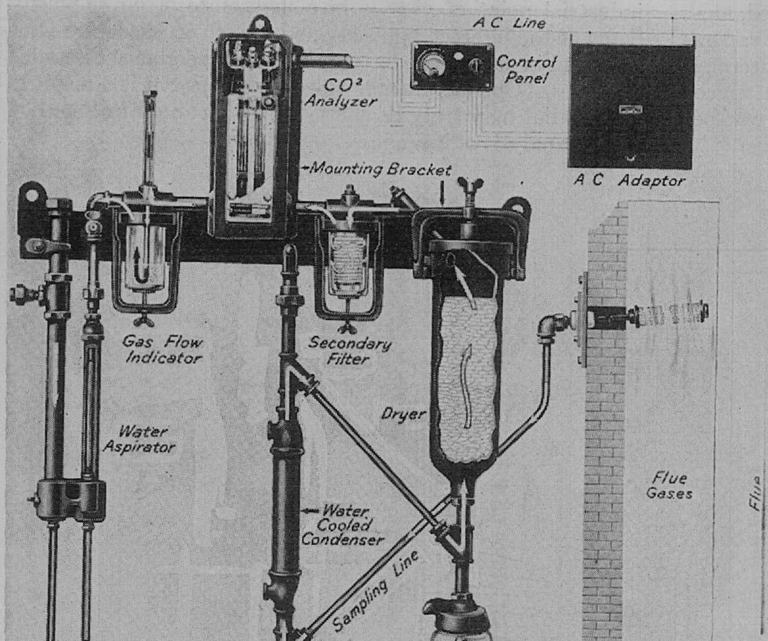
Figure 28 (*Left*). Micromax Carbon Dioxide Recorder–Thermal Conductance Cell

Courtesy, Leeds & Northrup Co.



Courtesy, Leeds & Northrup Co.

Figure 29. Micromax Carbon Dioxide Recorder



Figures 38 to 41 show the photoelectric scanning of the flame issuing from a Bessemer converter. Careful spectrographic studies (Figure 38) show that a useful correlation can be obtained between the incandescent gases and the correct blowing time of the converter. The locations of the photocell amplifier, recorder, and the flame target are shown in Figure 39. A complete record is shown in Figure 40, which after appropriate interpretation by the steel master gives a perfectly reliable indication of the condition of the charge.

This important investigation has been described in great detail on the basis of countless observations by Work (*303*), and its results have revived great interest in the Bessemer process.

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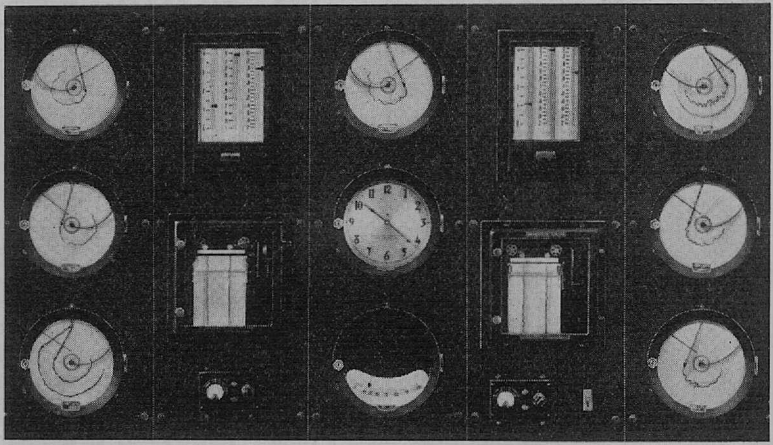
Figure 30. Schematic Diagram of Carbon Dioxide Analyzer Utilizing Thermal Conductance Principle

Courtesy, Brown Instrument Co.



Courtesy, Brown Instrument Co. and Glidden Co.

Figure 31. Flowmeters, Carbon Dioxide Recorders, Draft Gages, and Preheated Air and Feed Water Temperature Recorders on Control Panel

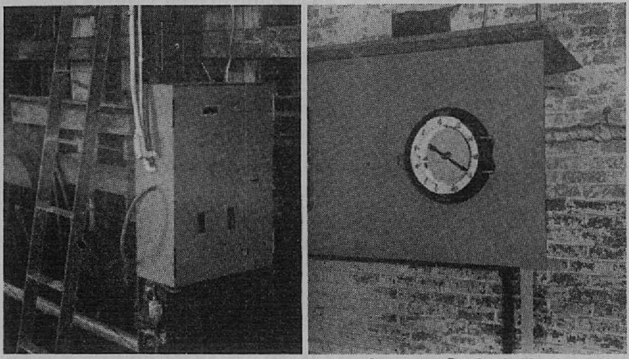
Spectroscopic

An index to the literature on spectrochemical analysis from 1920 to 1939 lists 1446 references (*190*). As the authors of this valuable compilation point out, as late as 1910 it was believed that these methods were of little qualitative value and that quantitative spectrochemical analysis had shown itself as impractical. In addition to about 30 textbooks and manuals on the subject, a number of compilations and bibliographies cover the subject fully (*13, 34, 242, 256, 257, 280, 281*). A very fine approach for the student or beginner is to be found in Brode's text (*30*), which gives a very thorough treatment of the theory, instrumental methods, and applications of spectroscopic methods as well as detailed directions for representative experimental work.

It may suffice here to outline the main features of modern spectroscopic work and to indicate some of the uses which have been made of this very valuable technique.

Theory. The contributions which spectroscopy has made to our knowledge of the universe range from astrophysics to the energy states in atoms. We are concerned here with the analytical information which they can furnish. The methods are applicable from the infrared to the x-rays.

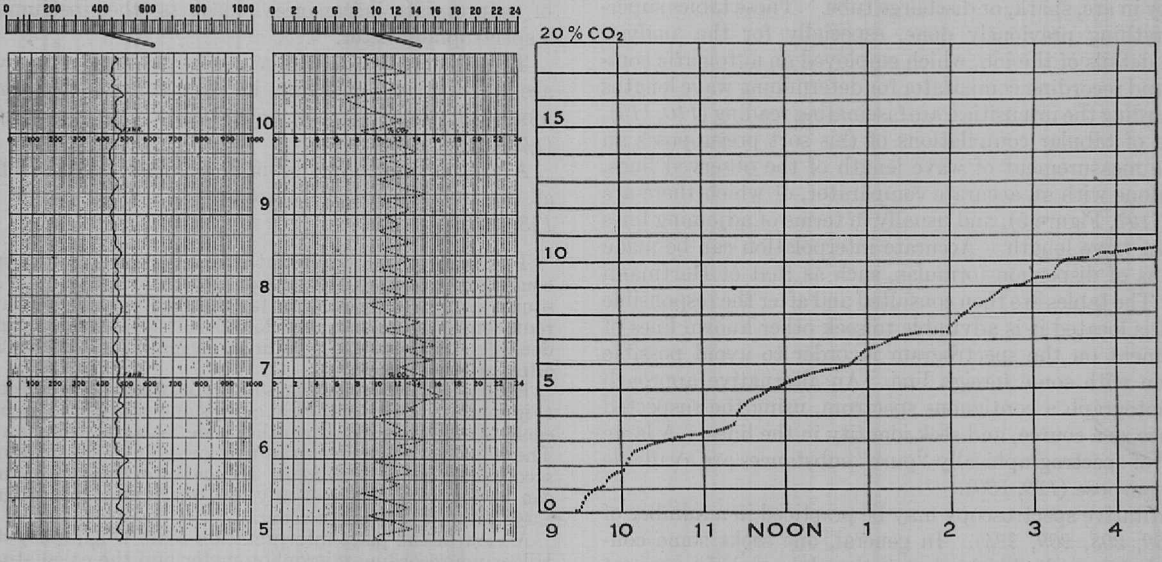
Emission Spectra. Under suitable conditions of excitation, atoms can be made to undergo definite electronic transitions which are followed by the emission of characteristic spectral lines. The lines are absolutely characteristic of an element and the certainty associated with this fact makes spectroscopy one of the most reliable means of identification known. The wealth of lines, particularly those due to iron, nickel, tungsten, and many other elements, may cause some confusion, and indeed, skill and experience are required to avoid this complication. (Toxicologists and spectroscopists



Courtesy, Leeds & Northrup Co.

Figure 32. Sulfur Dioxide Recorders

Measuring cell assembly (*left*) detects per cent of sulfur dioxide in continuous sample of flue gas from sulfur burner.
Micromax recorder (*right*) indicates and records per cent sulfur dioxide in flue gas from sulfur burner.



Courtesy, Brown Instrument Co.

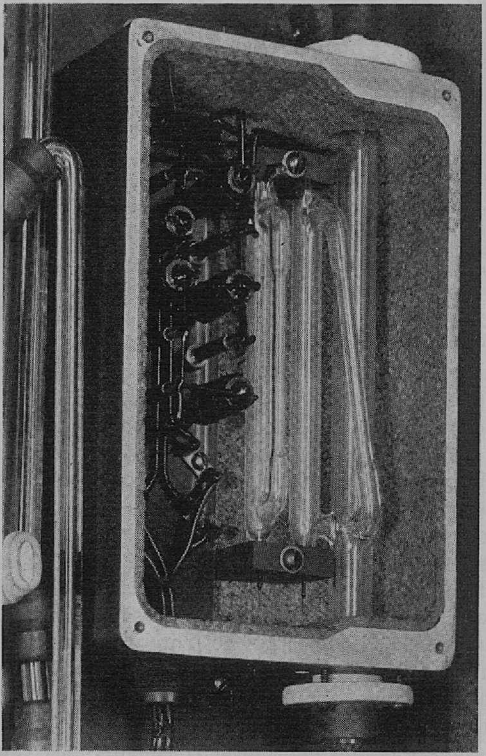
"From Dayne's Gas Analysis by Measurement of Thermal Conductivity"

Figure 33. Gas Analysis by Thermal Conductance Measurements

(*Left*) Carbon dioxide analysis from flue gas of a 250-horsepower boiler unit
(*Right*) Respiration of a single housefly (*Diptera domesticus*)

were amused some years ago in New York when one of the prominent iron lines was mistaken for that due to a relatively rare and highly toxic metal.)

The classification of spectral lines has occupied the attention of spectroscopists for many years. One of the finest compilations is the M. I. T. Wavelength Tables (*111*), which contains 109,275 entries giving the wave length, and the intensity in arc, spark, or discharge tube. These tables supersede anything previously done, especially for the analyst, and the details of the job, which employed an automatic computing and recording comparator for determining wave lengths and recording the intensities, are fascinating reading (*110, 113*). The use of tabular compilations of this sort presupposes an accurate measurement of wave length of the observed lines. This is done with an accurate comparator, of which there are several (*197*, Figure 5), and usually in terms of adjoining lines of known wave length. Accurate interpolation can be made by means of dispersion formulas, such as that of Hartmann (*109*). The tables are then consulted and after the responsible element is located it is advisable to seek other known lines of this element on the spectrogram in order to avoid possible confusion with some foreign line. An alternative approach is to photograph a contiguous spectrum, using the suspected substance as a source, and seek identity in the lines. A large number of spectrographically "pure" substances are available for this purpose (*129, 130*).



Courtesy, Leeds & Northrup Co.

FIGURE 34. ALL-GLASS THERMAL CONDUCTANCE CELL

Quantitative spectroscopy may be practiced in a number of ways (*59, 208, 209, 224*). In general, one seeks some connection between the blackening of the plate and the amount of the substance whose spectrum has been excited. A few of the methods may be mentioned; each has its proponents and enthusiasts and volumes have been written on the subject.

1. The use of standard samples containing known amounts of the desired constituent. These and the unknown sample are excited and photographed under identical conditions.
2. The "internal standard" method of Gerlach, in which (*91*) the intensities of the lines in the known and unknown are referred to some common line of an extraneous element which remains unchanged in both spectra.
3. The use of homologous pairs (*91*).

With all these methods the intensity of the lines is measured with a densitometer, examples of which have been described (*197*, Figures 56 to 59); other examples are shown in Figure 48.

INSTRUMENTS AND METHODS. Spectrographs with a prismatic dispersion and dispersion by means of gratings are available in all sizes and types, representative examples of which are shown in Figures 42, 43, and 44. The question of "size" in a spectrograph is determined largely by the nature of the problem. For many purposes, particularly in the nonferrous field, moderate dispersion is satisfactory, but for complex spectra, especially in the ferrous alloys, the highest dispersion is essential. The grating is preferred by many on account of its practically uniform dispersion throughout the spectrum. The relative merits of the two are discussed in standard texts.

Excitation Sources. The spectrum of the sample may be excited in the direct current arc, in the alternating current arc or spark, by the Abriss-Bogen or interrupted arc, and by the acetylene flame (see also *33*). The direct current arc, especially by arcing the sample to exhaustion, affords one of the most sensitive methods. The alternating current arc is more easily controlled, yet retains some of the advantages of the direct current arc. Most of the newer offerings of equipment make provision for all the electrical modes of excitation (Figure 45). An interesting trend is also observable in the number of completely coordinated assemblies which are offered for routine and research work (Figures 46, 47, and 48). It is becoming increasingly apparent to instrument manufacturers that a complete line of instruments for spectrographic analysis is of great advantage and convenience to the customer, and that for continuous routine work he should be furnished with a spectrograph, easily adaptable excitation equipment, densitometer, and other auxiliaries. Most instruments have also been designed with the thought of adapting them to related problems, such as absorption work. This is exemplified by the illustration of spectrophotometry, in which the addition of appropriate accessories converts the instrument into a spectrophotometer.

The numerous illustrations (Figures 49 to 52) given here are intended to illustrate in part correct and convenient modes of installing such apparatus for maximum efficiency (*142, 143*).

A view of the source room in the spectroscopy laboratory at the Dow Chemical Company is shown in Figure 53 (*142, 143, 232–4*).

This fireproof room houses the transformers, motor generators, condensers, resistors, synchronous interrupter, and other auxiliary source equipment necessary for the 35,000-volt alternating current condensed spark, two 25,000-volt alternating current condensed sparks, two 220-volt direct current arcs, and two 2200-volt alternating current arcs.

Each of these excitation sources is wired to a selector panel (Figure 54). One receptacle carries one side of the secondary of each of the sources, the other side being a common ground. The smaller receptacle carries two low-voltage leads for operating a contactor for each source. By means of this panel any source can be made available at any one of the four spectrographs located around the source room.

A view of the plate-interpretation room (Figure 55) shows the Hilger nonrecording microphotometer and the calculating board, used to convert microphotometer readings to per cent of the element in question.

Figure 56 is a view of one of the Bausch & Lomb medium quartz spectrographs. In addition to the spectrograph there is to be seen the outlet panel on which are mounted the control switch, warning lights, and double range ammeter, in addition to the power outlets.

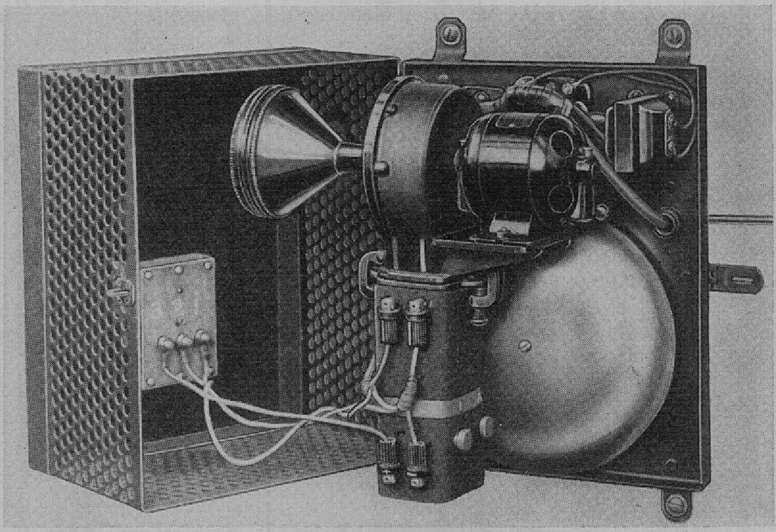
A similar outlet panel is located above the source tables before the other Bausch & Lomb medium quartz instrument, the Gaertner quartz Littrow, and the Cenco Replica grating instrument.

APPLICATIONS. For the countless applications of emission spectroscopy the reader must be referred to the copious references in the compilations quoted. They cover every conceivable field of analysis, from the examination of alloys, works of art, biological fluids, foodstuffs, toxicological (*37, 38*) and forensic specimens, to products of combustion, gases in internal combustion engines, fuels, glass, plants, and water analysis.

PRECISION, RAPIDITY, AND COSTS. It is not unnatural for the beginner or prospective spectroscopist to raise questions of precision, rapidity, and costs. A glance at any spectrographic laboratory will tell him that this is very expensive and elaborate equipment and although the wide range of applicability may be evident, he is interested in a definite answer to these questions. Since spectroscopic methods are among the most delicate which we have, and combine with a high degree of certainty and reliability, it is worth noting at the outset that the precision even for minute traces is rarely less than 10 per cent; and with the very best resources of densitometry

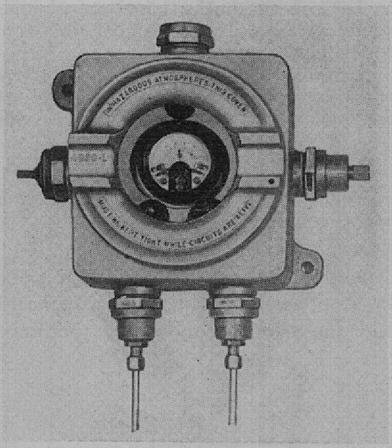
Courtesy, Mine Safety Appliances Co.

FIGURE 35. (*Upper Left and Lower Right*) EXPLOSIMETER. (*Center*) COMBUSTIBLE GAS INDICATOR. (*Lower Left*) GAS INDICATOR. (*Upper Right*) CARBON MONOXIDE INDICATOR



Courtesy, Mine Safety Appliances Co.

FIGURE 36. CARBON MONOXIDE ALARM AND VENTILATION CONTROL



Courtesy, Mine Safety Appliances Co.

FIGURE 37. EXPLOSION-PROOF COMBUSTIBLE GAS ALARM

and under carefully controlled conditions may be made as high as 2 or 3 per cent. Concerning the rapidity of the methods much has been said and published, but in the early days of quantitative spectroscopy it was shown by Meggers (*190*) that a series of analyses which required a full day's work by conventional chemical methods could be accomplished in less than 2 hours spectrographically and with no particular sacrifice in precision. The rapidity of the method must be gaged on the assumption of very careful preliminary development of the method and operating conditions. It is essentially in routine examinations that the economy in time becomes more and more apparent. In many procedures by the judicious apportioning of the work it has been possible to reduce quantitative analyses to a few man-minutes per determination.

Costs must be appraised on the same basis, especially in view of the high initial cost of the equipment, but here again experience has shown on numerous occasions that the costs can be brought even below those of conventional methods. Again in routine work it is apparent that cost and speed are interrelated and an increase in the former implies a certain reduction in the latter.

The present enormous industrial activity will undoubtedly produce new and startling figures bearing on these questions.

Absorption Spectroscopy–Spectrophotometry

Spectrophotometry is concerned with measurement of the amount of light absorbed or reflected at each wave length through the spectrum. It may be applied to the visible, ultraviolet, or the infrared. It will be more convenient to discuss the latter separately, although the laws applying to it are the same.

The law applying to the absorption of light at each wave length is that of Lambert and Beer.

The transmission, T, is defined as the ratio of the emergent intensity, I, to the incident intensity, I_0. For a solution containing a light-absorbing species of concentration c, in a layer of thickness t, we have the relationship:

$$I = I_0 \times 10^{-kct} \tag{1}$$

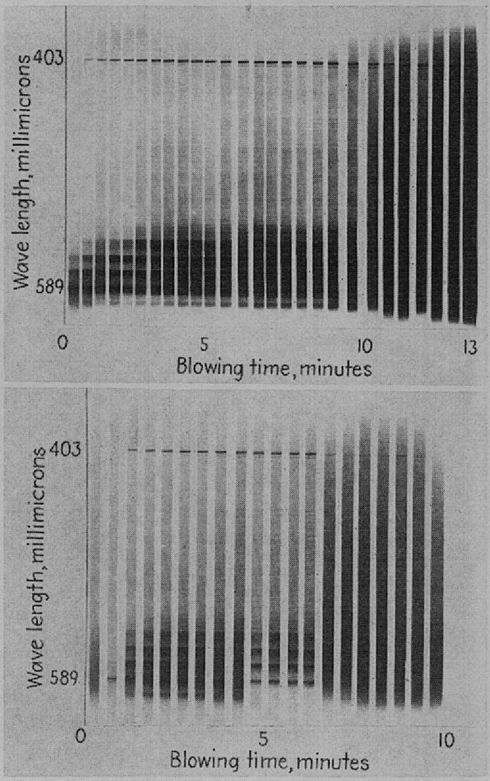
from which we may write

$$-\log I/I_0 = kct = -\log T \tag{2}$$

or

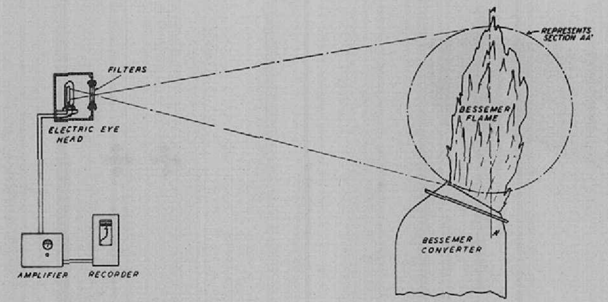
$$\log I_0/I = kct = E \tag{3}$$

where E is the extinction, E/t is the extinction coefficient, and k is the molar extinction coefficient, provided c is expressed in moles per liter. There is no particular uniformity in terminology or symbols in this field and it is still necessary for investigators to report the meaning of the symbols which they employ and the units in which they are expressed. Some investigators have used the term density, D, instead of extinction, E. The use of E conforms more nearly with European practice and D seems to have



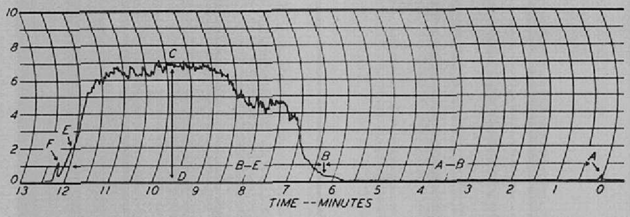
Courtesy, H. K. Work, Jones and Laughlin Steel Corp.

FIGURE 38. SPECTROGRAMS OF BESSEMER FLAME AS A FUNCTION OF BLOWING TIME



Courtesy, H. K. Work, Jones and Laughlin Steel Corp.

Figure 39. Schematic View of Photoelectric Bessemer Flame Scanning



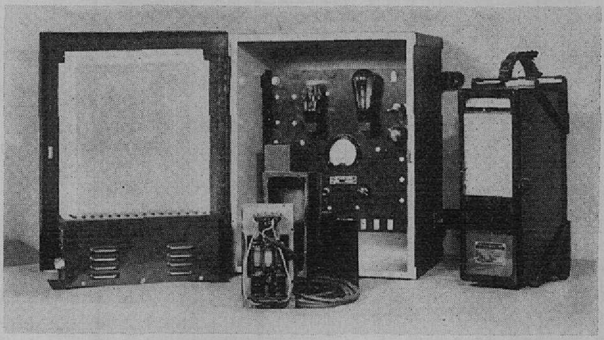
Courtesy, H. K. Work, Jones and Laughlin Steel Corp.

Figure 40. Automatic Record of Bessemer Blow

been borrowed from the field of photographic densitometry, where it is used to give an exact expression for the blackening of a plate.

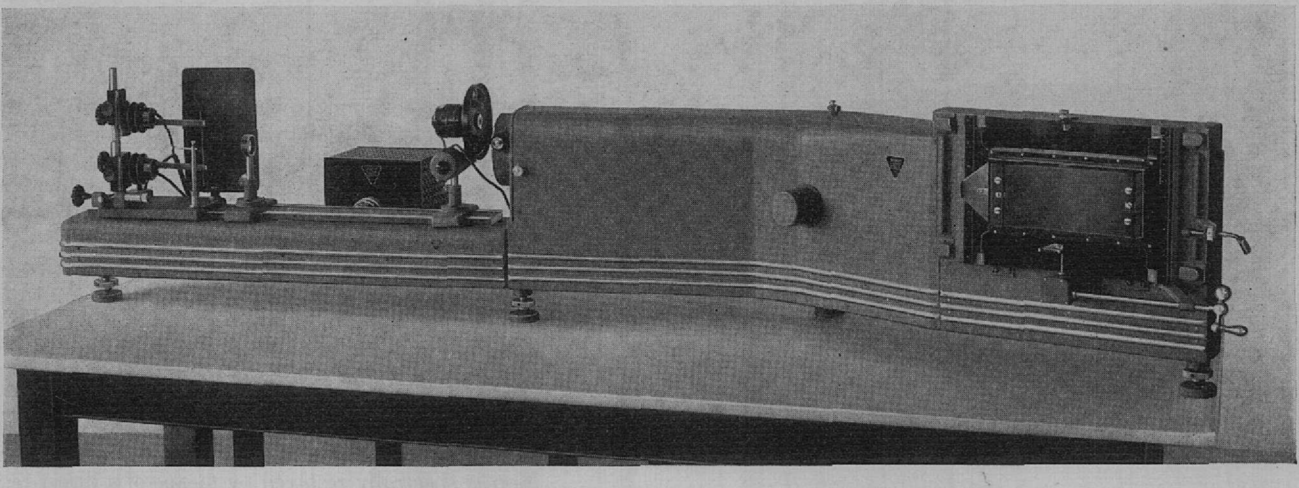
The foregoing discussion of extinction and extinction coefficients implies a definite wave length, λ. Indeed, the variation of extinction with wave length is the only fundamental way of expressing the "color" of a light-absorbing substance and a curve relating extinction to wave length gives us the absorption spectrum or characteristic color curve. To be sure, in most measurements the transmission is measured directly and the extinction or extinction coefficient must be computed from the transmission data. It can be shown that if one plots log extinction as a function of the wave length, such curves will be still more useful from the point of view of identifying a colored substance. Such curves are independent of the concentration and thickness and can be superimposed by a shift along the ordinate (log E) axis. This is shown very nicely by Figure 57 (upper)[1], which shows the log extinction curves for a dye notorious for its deviation from Beer's law. The curves are taken at six different concentrations (1.25, 2.5, 5, 10, 20, and 40 mg. per liter), and should be directly superimposable by shifting them along the ordinate axis if the typical "color" is independent of concentration. That this is not the case for this substance is shown in the lower graph, which illustrates the failure of Beer's law except at a pivotal wave length of approximately 552 millimicrons. This shows the Beer's law can be applied with confidence at this wave length but would be highly in error at others, particularly at the longer wave lengths.

Very frequently elaborate series of transmission curves are presented to illustrate changes in the absorption of a substance, but they are almost useless in that form for any accurate appraisal of the changes unless they are recalculated to the log E basis. To be sure, the point-by-point recalcula-



Courtesy, H. K. Work, Jones and Laughlin Steel Corp.

Figure 41. Photocell Head, Amplifier, and Recorder for Control of Bessemer Steel Making



Courtesy, Bausch & Lomb Optical Co.

Figure 42. Spectrograph

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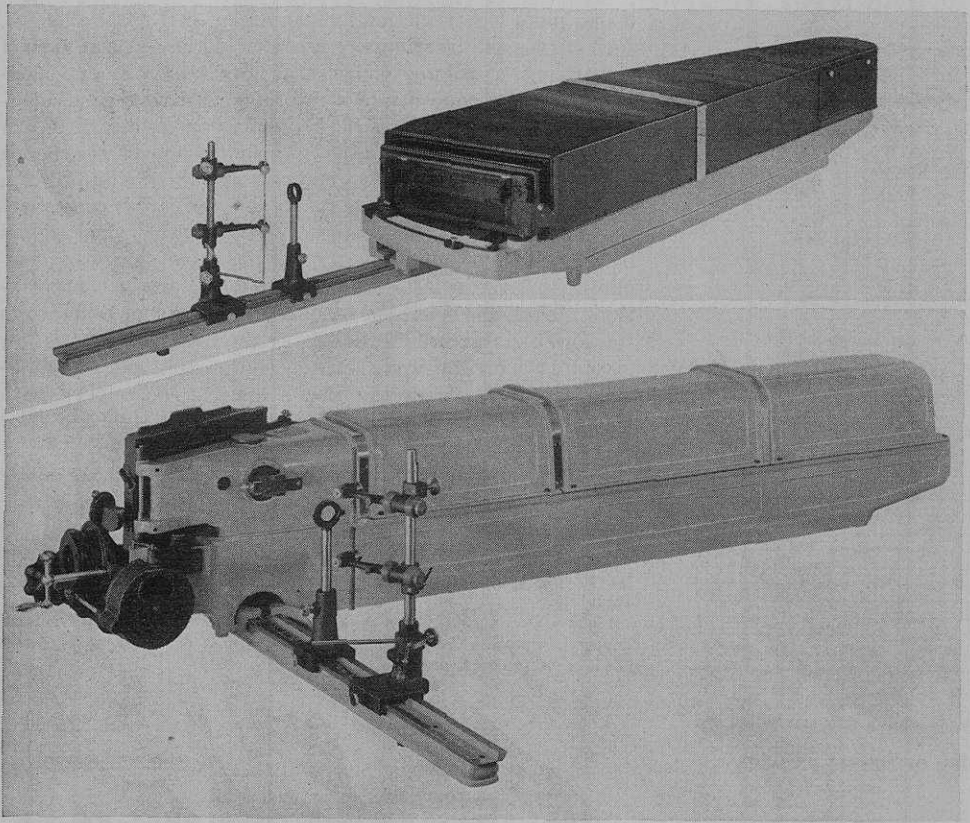
[1] The writer is greatly indebted to W. A. Shurcliff of the Calco Chemical Division, American Cyanamid Company, for the preparation of the curves in Figure 57, to illustrate this important principle.



Courtesy, Jarrell-Ash Co. and Adam Hilger, Ltd.

FIGURE 43. (*Upper*) TECHNICAL GRATING SPECTROGRAPH. (*Lower*) FULLY AUTOMATIC LARGE QUARTZ AND GLASS SPECTROGRAPH

* *

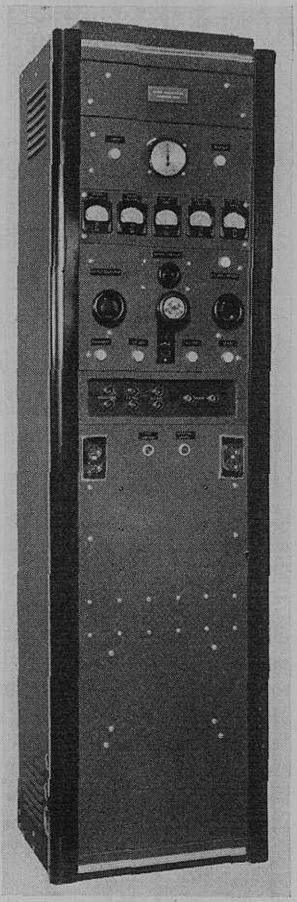
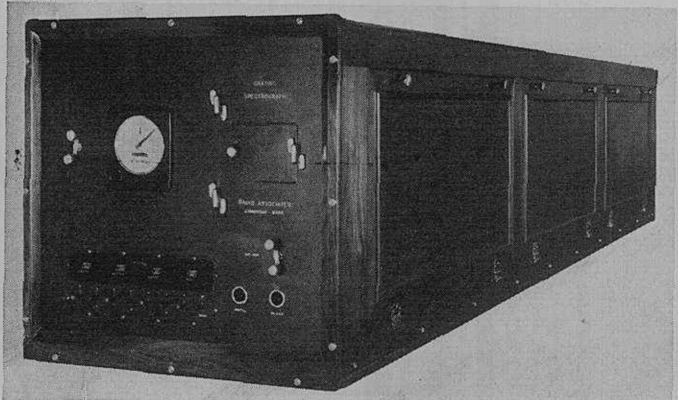


FIGURE 45. CONTROL PANEL FOR SPECTROGRAPH EXCITATION EQUIPMENT

Courtesy, Baird Associates

tion is laborious, but in the case of recording spectrophotometers the labor is completely eliminated by the introduction of a log log $1/T$ cam (Figure 58) with which curves similar to Figure 57 are obtained.

Analytical interest resides in the fact that for systems obeying Beer's law a plot of extinction against concentration is linear. In seeking the conditions under which this useful relationship may be obtained the importance of the log E curves is once more evident, in that if the curves are completely superimposable Beer's law will hold at any wave length. If there is a common point, as in Figure 57 (lower), that wave length alone will be satisfactory. In the former case the principal advantage lies in the fact that one has complete freedom of choice, which may be very useful if other light-absorbing species are present.

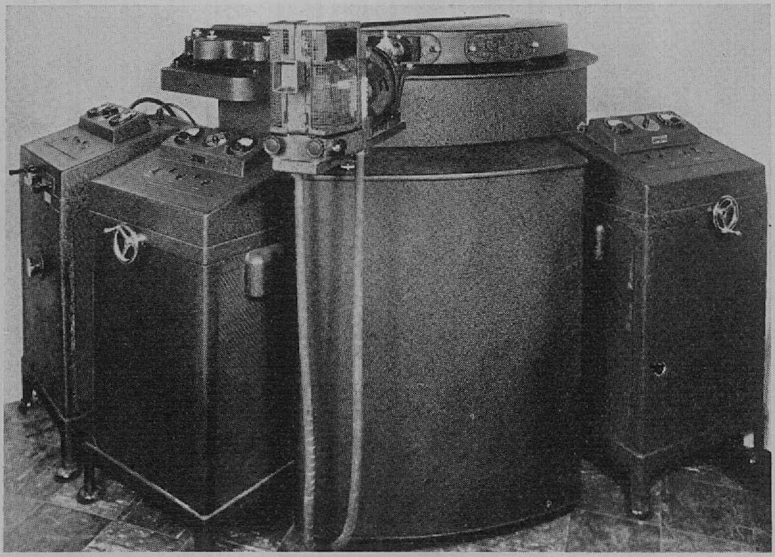


Courtesy, Baird Associates

FIGURE 44. THREE-METER GRATING SPECTROGRAPH

The analysis of mixtures is spectrophotometrically feasible, since the extinctions are additive and the method merely presupposes that there is no interaction between the two light-absorbing entities. The theory of this and the other topics discussed here is covered in standard references (*30, 114*).

INSTRUMENTS AND METHODS. *Visible Spectrum.* In all spectrophotometers a source of continuous radiation is spectrally resolved by means of a direct-reading spectrometer or monochromator, either before or after the photometric matching.



Courtesy, Harry W. Dietert Co.

FIGURE 46. SPECTROGRAPH ON METAL BASE WITH THREE SOURCE UNITS

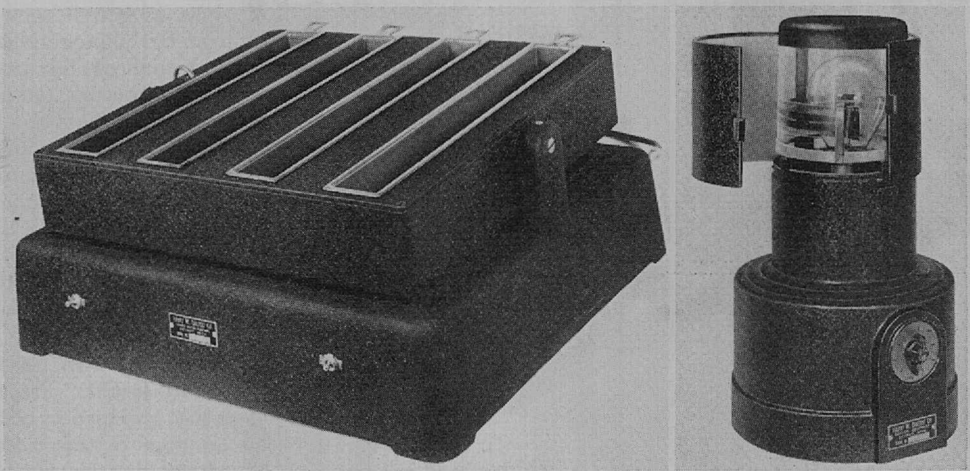
1. The Polarization Type. In this class the measuring beam and the comparison beam are matched for equal intensity by reducing the intensity of the comparison beam by a polarizing mechanism (*294*). The decrease in intensity is a trigonometric function of the angle of rotation of the polarizing element. It is specifically in terms of two match points. The transmission is given by $T = \cot^2 \theta \times \tan^2 \varphi$ where θ is the larger angle; or if sample and solvent are interchanged and the measurement is repeated, the transmission is given by $T = \cot \theta \times \tan \varphi$. Examples of this class are the Königs-Marten, Bausch & Lomb (Figures 59, 60, and 61), and Nutting (Hilger). As a rule the scale attached to the polarizer head is calibrated to read the angle in degrees, another portion is engraved in transmission, and a third in extinction values. This is a widely used and time-honored type. The only drawback is the caution which must be exercised in measuring the reflectance of samples which might give rise to polarization effects due to surface structure or other causes.

2. Sector Type. In this instrument the photometric matching is achieved by varying the aperture of a rapidly rotating sector while it is in rapid motion. The rotational rate of the sector is high enough to eliminate any perceptible flicker. The scale usually reads directly in transmission values which are really given by the effective opening of the sector and can be measured mechanically with a high degree of precision. An example of this class is shown in Figure 62.

3. Photoelectric Spectrophotometers. In these the relative intensity of the measuring and reference beams are measured photoelectrically following the spectral resolution of the beams (Figure 63). Two manually operated examples of this class have been described (*197*, Figures 63 to 66). A completely automatic instrument developed some years ago by Hardy is the General Electric color analyzer (Figure 64). This well-known instrument has been described in several places and many important researches have been based on its use. It operates on a strictly null principle in which the unknown and comparison beams are rapidly intercompared and a photocell-thyratron unit controls a motor which continuously rebalances the system. A complete spectrum may be recorded in from 2.5 to 5 minutes. Numerous attachments are available in the form of computed cams (Figure 58), whereby the results will be plotted as per cent transmission or reflectance, extinction or log extinction. A somewhat more complex attachment is available for computing trichromatic coefficients directly.

These instruments are all to be regarded as the fundamental standards for expressing "color" and are capable of high precision in the hands of an experienced operator (*108*, *109*). They have been used very extensively in chemical analysis. They are expensive by virtue of their elegance and precision, and for many analytical purposes some of the compromise instruments which are discussed below will do just as well. However, in any extended program of work one has constant and repeated need for recourse to this important instrument. The photoelectric type is not necessarily more accurate but does have unusual advantages in the extreme ends of the visible spectrum where the visibility function is poor.

Ultraviolet. Most of the information in this region can be obtained only by photographic or photoelectric means. Any spectrograph may be fitted with means of splitting the incident light into two beams, in one of which a sample is placed and in the other some intensity weakening mechanism is introduced. A common form of intensity reducer takes the



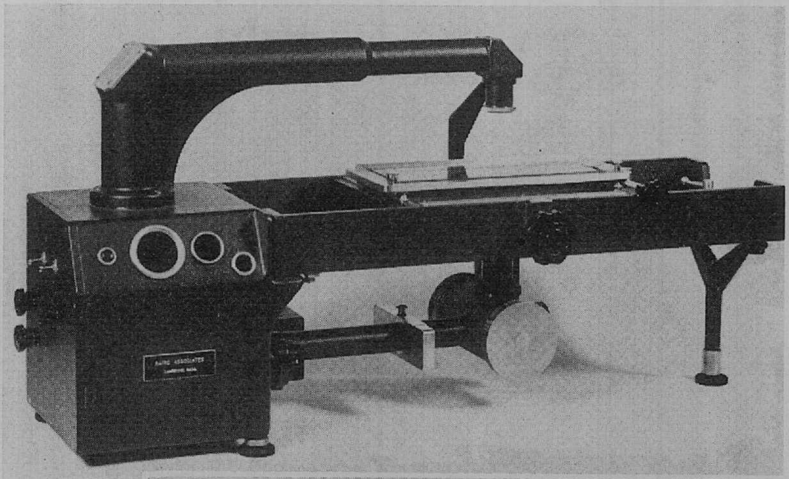
Courtesy, Harry W. Dietert Co.

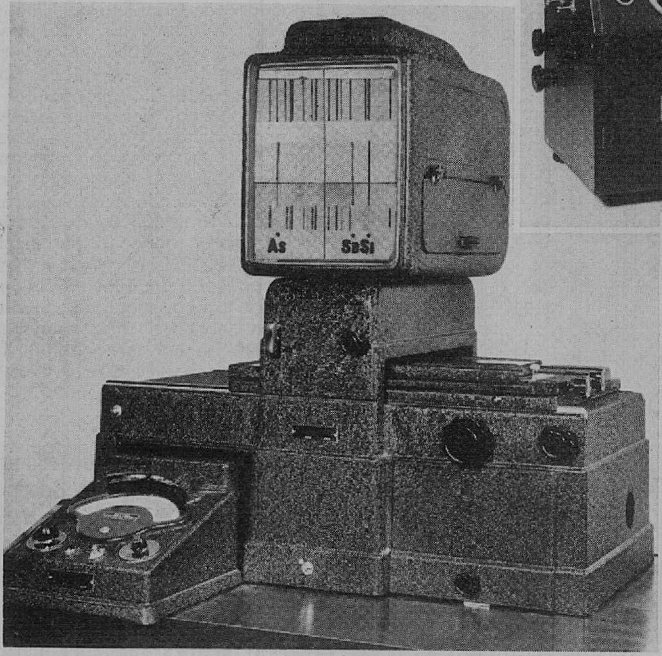
FIGURE 47. (*Left*) ARL-DIETERT FILM-DEVELOPING MACHINE. (*Right*) ARL-DIETERT FILM INFRARED FILM DRYER

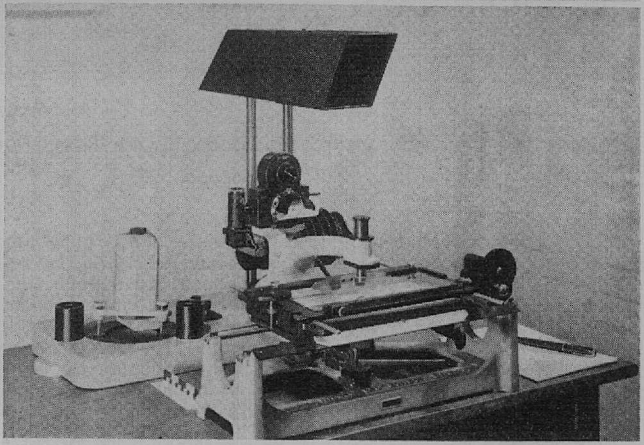
FIGURE 48. (*Lower Left*) COMPARATOR-DENSITOMETER
Courtesy, Harry W. Dietert Co.

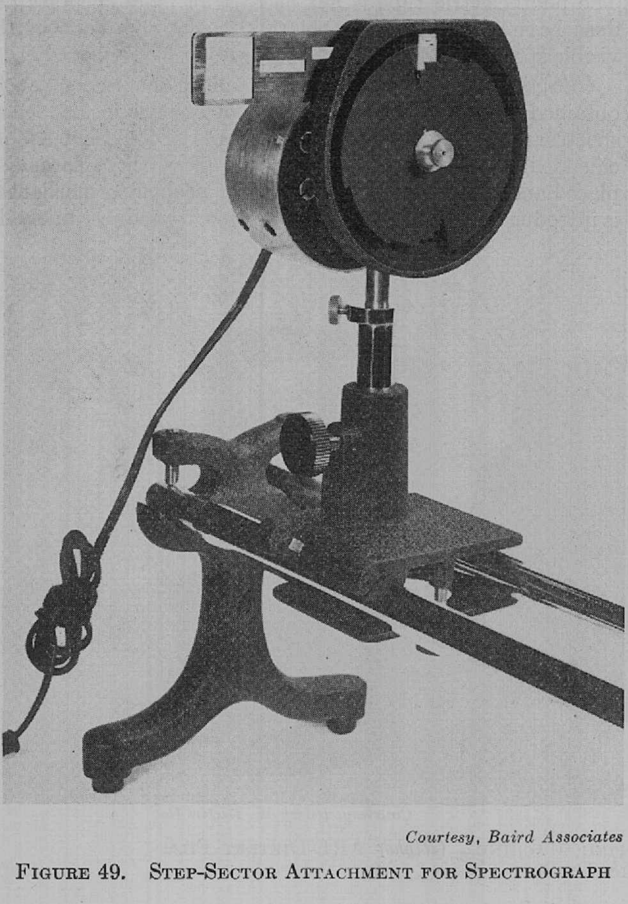
(*Upper Right*) NONRECORDING DENSITOMETER
Courtesy, Baird Associates

(*Lower Right*) MICROPHOTOMETER AND GALVANOMETER READER UNIT
Courtesy, Jarrell-Ash Co. and Adam Hilger, Ltd.









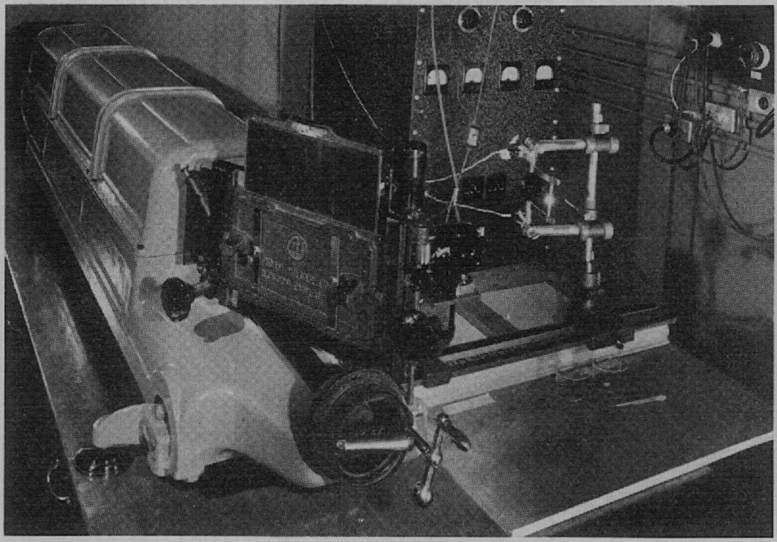
Courtesy, Baird Associates

FIGURE 49. STEP-SECTOR ATTACHMENT FOR SPECTROGRAPH

form of a rotating sector (Figure 65), and another of an adjustable diaphragm (Figure 66). If these pairs of spectra are photographed side by side and this process is repeated for an extended series of sector or diaphragm settings, the absorption curve is obtained from the spectrogram by noting the wave length at which intensity matches can be found (Figures 67 and 68). For careful work a series of spectra at various intensities can be recorded to calibrate the photographic plate itself, since, as is well known, the blackening-intensity relationship of the photographic plate is complex (*109*). An iron arc or an underwater spark may be used as the light source for this type of work, but a perfectly continuous source such as the hydrogen discharge tube is preferable. Measurements of this type are exact and furnish accurate extinction values, but for some semiquantitative results it is often feasible to make a single measurement through a solution and to record the intensities with a densitometer. A comparison record must be obtained for the source alone in order to lump or integrate the combined effects of energy distribution in the source and the characteristics of the plate.

Photoelectric instruments of two classes have been developed, manual and photoelectric. Precise examples of the former have been described by Hogness (*133*) and von Halban (*294*) and a recent addition to this class is illustrated by Figures 69 and 70. Recording instruments have been described by Harrison (*112*) and Brode (*30*).

The experimental difficulties attending the construction and use of these instruments are far greater than the corre-



Courtesy, Jarrell-Ash Co., Adam Hilger, Ltd., and Eastman Kodak Co.

FIGURE 50. FULLY AUTOMATIC LARGE QUARTZ AND GLASS SPECTROGRAPH

sponding problem in the visible, but so much valuable information is obtainable in the ultraviolet that the problem has rightly engaged the interest of many experts.

Other examples are illustrated in Figures 71 and 72.

APPLICATIONS. A recent compilation (*288*) lists 866 references to spectrophotometric investigations, covering analytical problems in every imaginable field: inorganic, organic, biological, metallurgical, and industrial (*191*, *202*). A few more or less generic or typical problems (*4*) include:

1. Characteristic identification (dyes)
2. Determination of mixtures
3. Study of equilibria (pH with indicators)
4. Confirmation of structure as a liaison medium between analysis and synthesis, an excellent recent example of which is the case of vitamin B_1 (*230*).

Infrared

The fundamental information which has been derived from the absorption of light in this region, together with the related information from dielectric measurements and Raman spectra, has contributed enormously to our knowledge of molecular structure. The great amount of data which has been accumulated primarily for this purpose is beginning to be used and appreciated for its analytical value and recently it has turned out that despite great experimental difficulties and complications this technique will have an almost revolutionary effect on the analytical chemistry of the future. Some of the finest resources of modern research have been directed precisely to this end.

A negligible portion of the infrared is accessible by photographic technique and it is necessary to measure the absorption in this region by receiving the spectrally resolved radiation on the surface of a sensitive thermopile. Until very recently it has been necessary to study absorption in this region by means of point-to-point measurements of thermopile-galvanometer readings throughout the spectrum. One of the useful characteristics of absorption in this region is the distinctive nature of many of the vibrational bands and their unmistakable association with definite atomic linkages—for example, in Table II, reproduced from Brode (*30*), definite frequencies can be associated with the indicated functional groups.

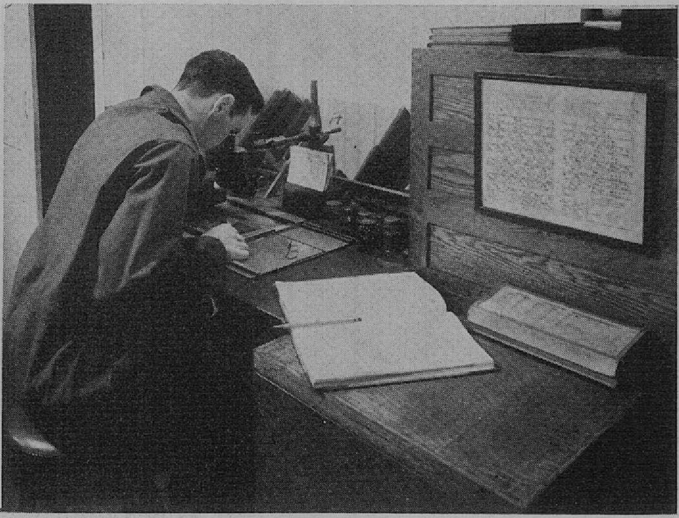
TABLE II. FREQUENCY VALUES FOR INFRARED ABSORPTION BANDS DUE TO INDICATED LINKAGES

Functional Group	Frequency, v' Cm.$^{-1}$	Functional Group	Frequency, v' Cm.$^{-1}$
≡C—H	2910	—S—H	2500
≡C—C≡	990	=N—H	3300
=C=C=	1630	≡C—I	500
—C≡C—	2200	≡C—B	560
=C=O (ketones)	1722	≡C—Cl	650
=C=O (acid)	1660	—C≡N	2250
≡C—N=	1035	—N≡C	2150
≡C—O—	1034	=N—O—	1003
—O—H	3380	—NH—NH—	3000

It is characteristic also that, especially in homologous series, the frequency does not shift greatly, but there may be very considerable intensity variations. For most analytical purposes one is not concerned with the subtler differences in band structure but solely with the general nature and frequency allocation.

Courtesy, Bell Telephone Laboratories

FIGURE 51. ANALYTICAL APPLICATION OF SPECTROGRAPH



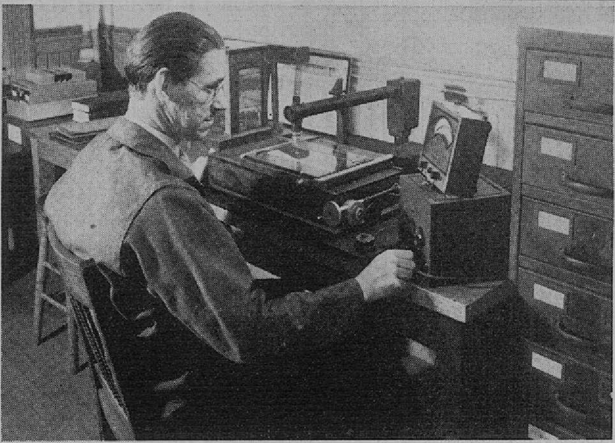


FIGURE 52. (*Upper Left*) INDUSTRIAL INSTALLATION USING LARGE LITTROW QUARTZ SPECTROGRAPH

Showing excitation stand and fume hood and controls. Utilizes direct current arc, high-voltage spark, and modified Feussner spark and disruptive spark

(*Upper Right*) VISUAL COMPARISON AND ANNOTATION OF PLATES

(*Lower Left*) DIRECT-READING MICROPHOTOMETER AND AMPLIFIER FOR SPECTROGRAMS

Courtesy, Lucius Pitkin, Inc.

◆

INSTRUMENTS AND METHODS. A typical arrangement for this class of measurement is illustrated in Figure 73.

Radiation from a Glo-bar source is passed to a series of mirrors which focus radiation on a narrow slit. The radiation proceeding from this slit is rendered parallel and strikes a rock-salt prism arranged in Littrow mounting. The dispersed radiation is reflected from the Littrow mirror, sent once more through the prism, and ultimately brought to focus on a thermocouple connected to a highly sensitive galvanometer.

So far the arrangement is representative of most infrared setups. Most earlier attempts to make the

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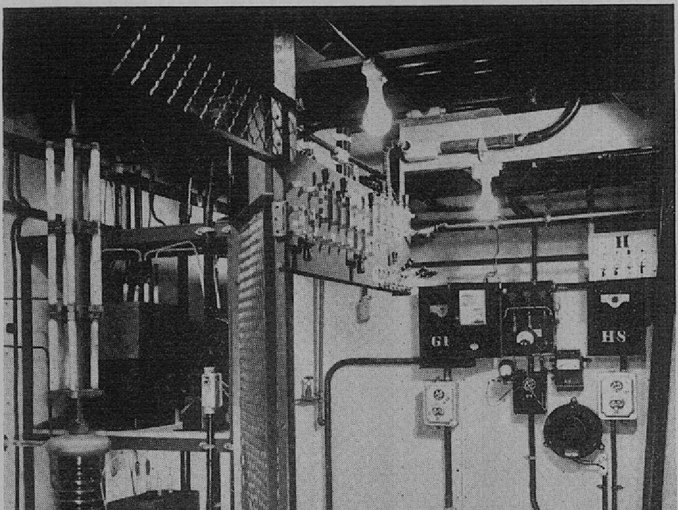
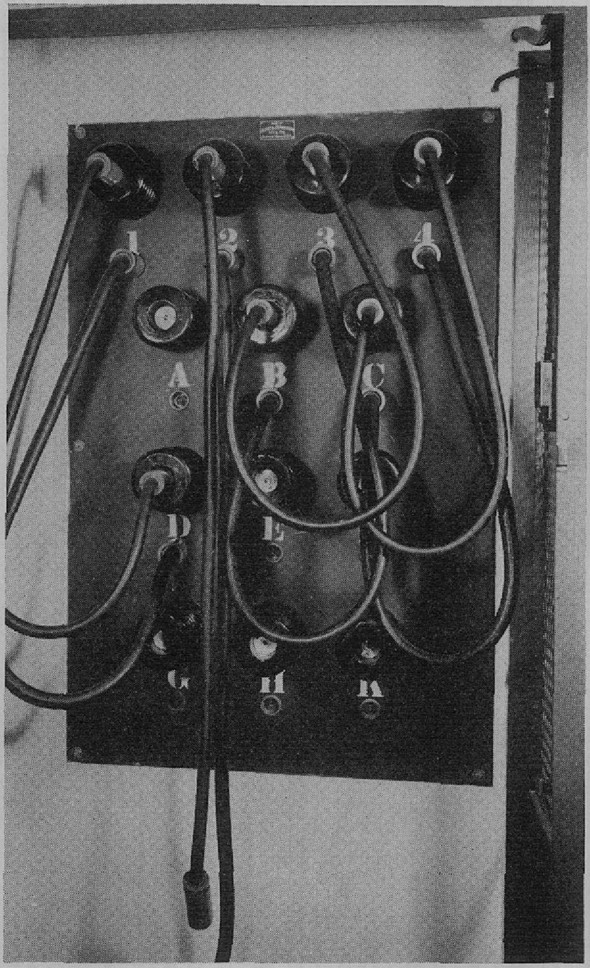


FIGURE 53. SOURCE ROOM, SPECTROGRAPHIC LABORATORY

Courtesy, Dow Chemical Co.



Courtesy, Dow Chemical Co.

FIGURE 54. SELECTOR PANEL FOR EXCITATION SOURCES IN SPECTROGRAPHIC LABORATORY

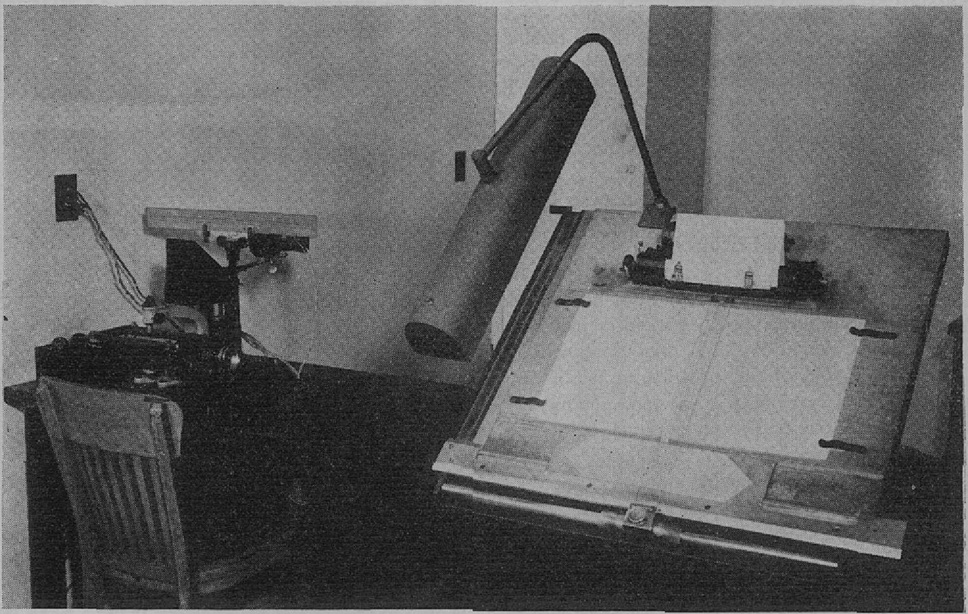
assembly automatically recording utilized photographic recording of the galvanometer deflections. The improvements in this particular installation provide electronic means for following galvanometer deflections.

A motor in the recorder unit slowly moves the dispersion train through a worm gear and sector, as shown in Figure 73, so that the entire spectrum from 2μ to 11μ is slowly swept across the exit slit. The same motor drives a drum in the recorder unit on which a large piece of graph paper is mounted. The deflection of the light beam from the galvanometer mirror is detected by means of a photoelectric follow-up mechanism: a photocell unit motor-driven in such a manner that it constantly "chases" the light beam. This unit also carries a pen or stylus which draws a line on the recorder paper. Thus a continuous curve is drawn, and is visible at all times to the operator, relating energy to wave length. If an absorbing substance (sample) is placed in the optical path of the spectrometer, the regions of characteristic absorption will appear in the record and simple computations from the record will reduce this curve to an equal energy base.

The data for more than 600 key organic compounds have been recorded with this instrument and even at this stage of progress give a quick and reliable answer to many important problems. Arrangements have been made for the detailed description and list of uses of this fine installation to appear in the ANALYTICAL EDITION. Some of its uses are illustrated in Figures 74 to 78.

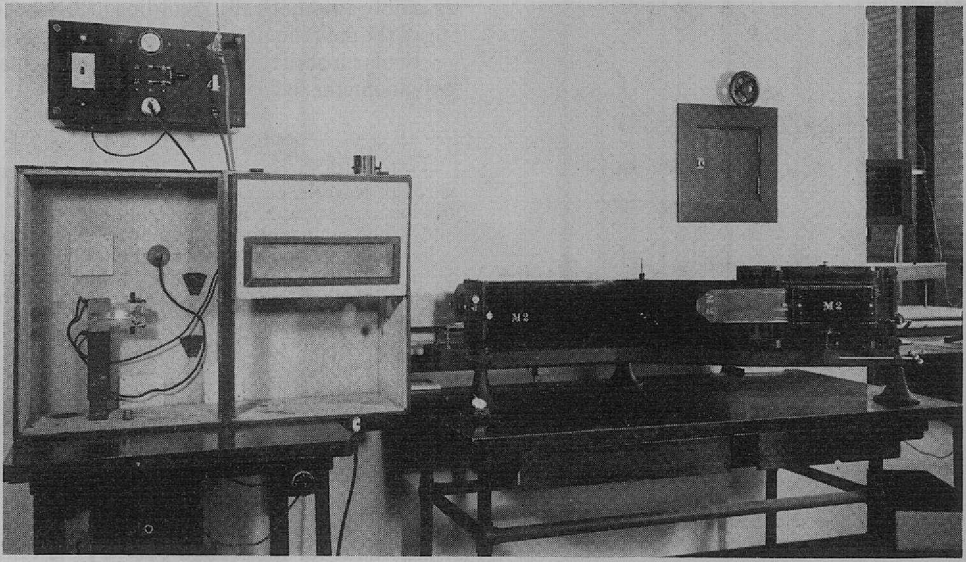
Figures 79 and 80 show two views of an automatic, recording infrared spectrometer with optical path enclosed in an air-tight case of Dowmetal. Although similar to a previously described instrument (*304*), it has a number of improvements.

It is equipped with exchangeable 60° prisms of rock salt and lithium fluoride which operate in a Littrow mounting. All controls of the apparatus are located at one end of the spectrograph within easy reach of a seated operator. Widths of the slits can be varied by turning a crank, wave lengths can be determined from



Courtesy, Dow Chemical Co.

FIGURE 55. PLATE-INTERPRETATION ROOM IN SPECTROGRAPHIC LABORATORY, WITH DENSITOMETER AND COMPUTING BOARD



Courtesy, Dow Chemical Co.

Figure 56. Quartz Spectrograph in Spectrographic Laboratory

a revolution counter, drive speeds can be easily changed by rearranging a belt and pulley system, and a radiation shutter can be opened or closed by turning a knob on the switch panel.

The galvanometer deflections can be followed visually on the ground-glass scale while being photographically recorded on the drum camera which is within the operator's reach. A separate air-tight case contains the Globar source and focusing mirror. This unit is made movable, so that all air space between it and the sample cells, which are of different thicknesses, can be displaced.

Typical results obtained with this type of instrument are shown in Figure 3 of Wright's paper (*304*).

Very useful results have been obtained without the use of a spectrometer by using a scheme proposed by Pfund. As used for the estimation of carbon dioxide, radiation from a hot carbon dioxide source (Bunsen burner) is passed through a cell to a receiver (thermopile) immersed in carbon dioxide. In the absence of carbon dioxide in the absorption tube the receiver heats up as a result of absorption of the radiation selectively emitted by the source. In the presence of carbon dioxide in the absorption tube, the heating of the receiver is diminished. This method should be applicable to all gases which can be caused to emit the infrared radiation which they absorb.

Applications. It can be inferred from Table II that the number of compounds which can be investigated by this powerful tool is almost unlimited and the systematic accumulation of data which is now proceeding rapidly in many places will eventually lead to a convenient form of classification from which direct analytical information may be deduced with ease. One is not to infer that we are only now in a position to learn something about the infrared; that process has been going on for years, but with the increasing realization of the distinctive analytical use the classification and interpretation will be directed to those uses.

There is a high degree of specificity and certainty about these measurements; they can be extraordinarily sensitive as well—for example, it is possible to determine accurately as little as one part of water in a million parts of carbon tetrachloride which possesses no bands interfering with the water band. A number of applications have been described recently by Wright (*304*).

Courtesy, W. A. Shurcliff, Calco Chemical Division, American Cyanamid Co.

Figure 57. (*Above*) Log Extinction Curves for Calcocid Violet 4BX. (*Below*) Log Extinction Curves Adjusted Vertically by Concentration Factors

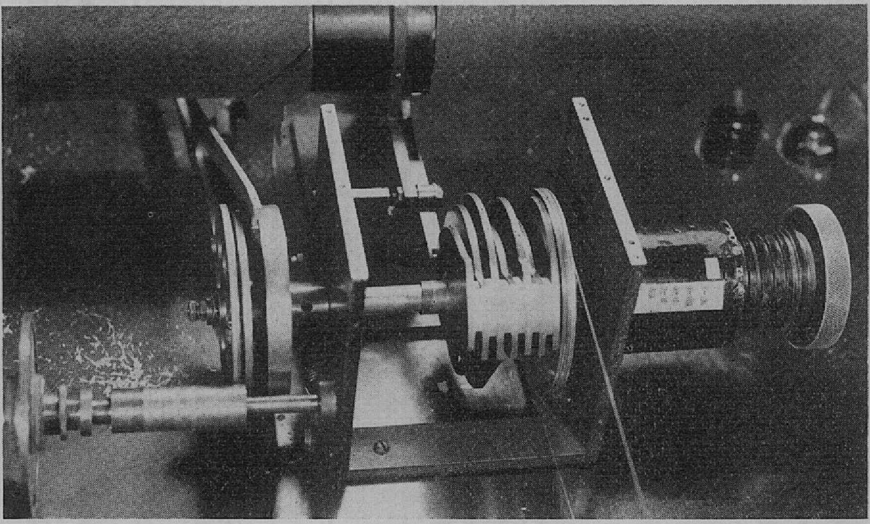


FIGURE 58 (*Above*). SPECTROPHOTOMETER CAM ASSEMBLY

Log log $1/T$ cam on right

Courtesy, W. A. Shurcliff, Calco Chemical Division, American Cyanamid Co.

Raman Spectra

The information afforded by Raman spectra is closely related and complementary to that derived from infrared studies. The Raman effect is based on the observation that the light scattered from molecules which are illuminated with monochromatic light contains frequencies that were not present in the incident radiation. The differences in frequencies correspond to definite energy states in the molecules and are therefore characteristic of the structure of the particular molecule. One great advantage of the Raman technique is that one works in a photographically accessible region and therefore has that advantage over the complicated technique necessary in the infrared. Since the Raman scattering is very feeble, the necessary exposures are rather long.

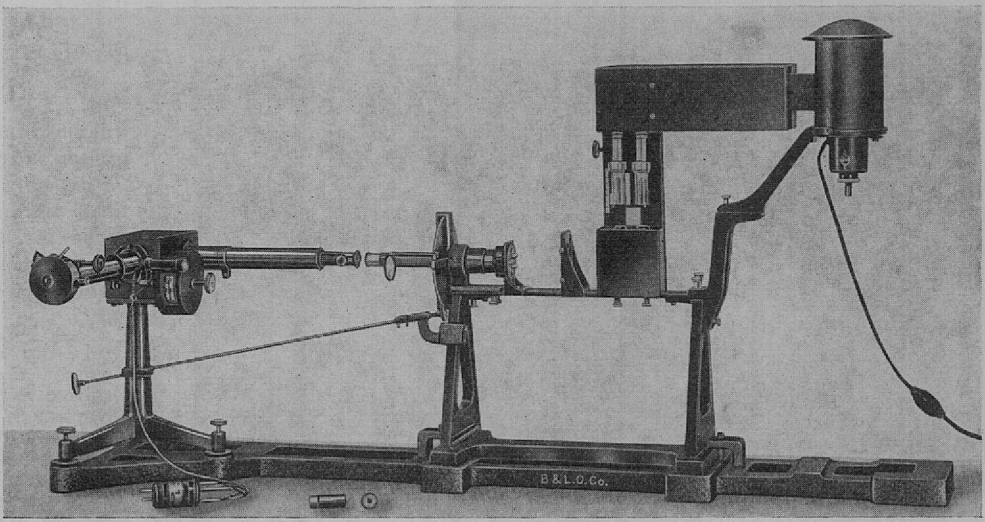


FIGURE 59 (*Right*). POLARIZATION-TYPE SPECTROPHOTOMETER

Courtesy, Bausch & Lomb Optical Co.

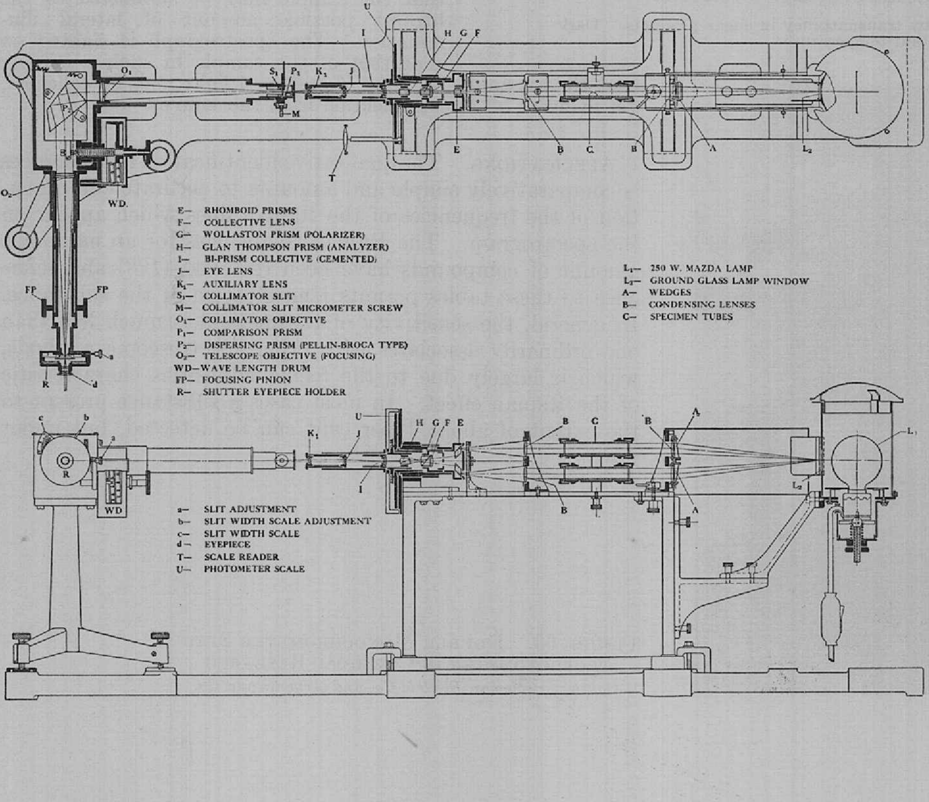
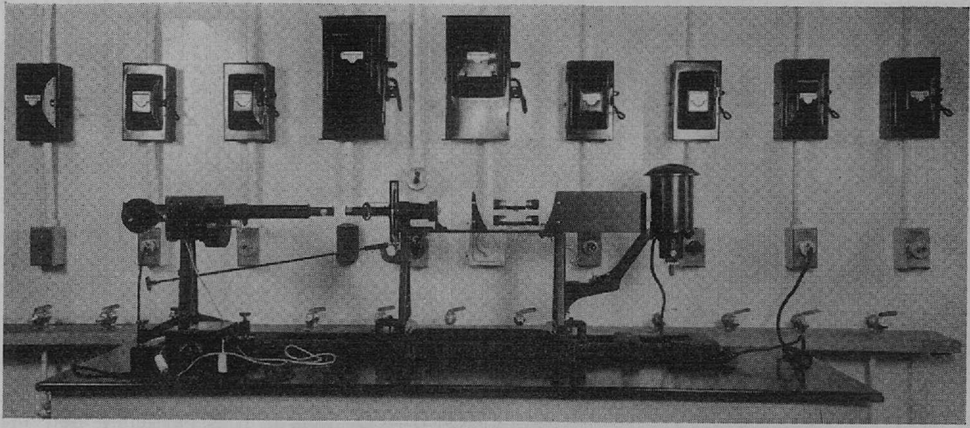


FIGURE 60 (*Below*). POLARIZATION-TYPE SPECTROPHOTOMETER

Courtesy, Bausch & Lomb Optical Co.

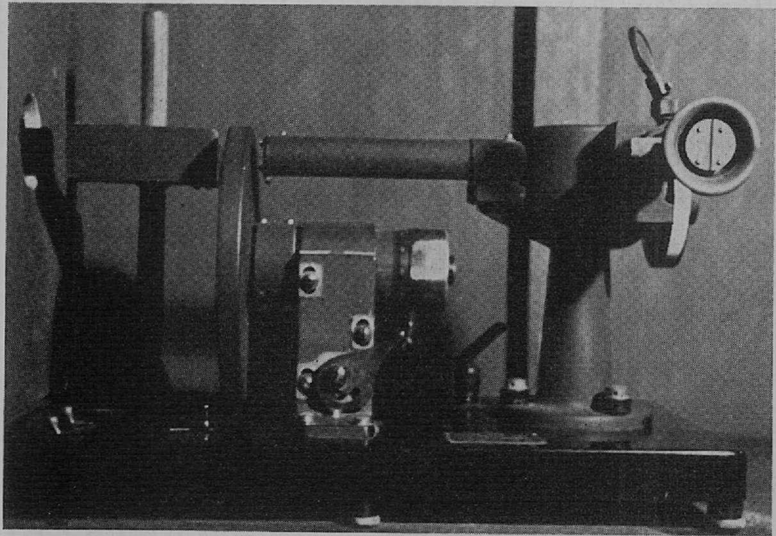
An enormous amount of information has been accumulated in the 13 years since the discovery of the phenomenon and there are several excellent monographs on the subject (*100, 128*).

INSTRUMENTS AND METHODS. The equipment for obtaining Raman spectra is described in great detail in several textbooks. The method consists, in general, of some means for subjecting the substance to intense illumination with



Courtesy, G. I. Lavin, Rockefeller Institute for Medical Research

FIGURE 61. SPECTROPHOTOMETER FOR VISIBLE REGION (BAUSCH & LOMB)



Courtesy, F. W. Zerban, New York Sugar Trade Laboratory

FIGURE 62. KEUFFEL AND ESSER SPECTROPHOTOMETER

Used for color and turbidity determinations by transmittancy in sugar products. Dark room held at constant temperature

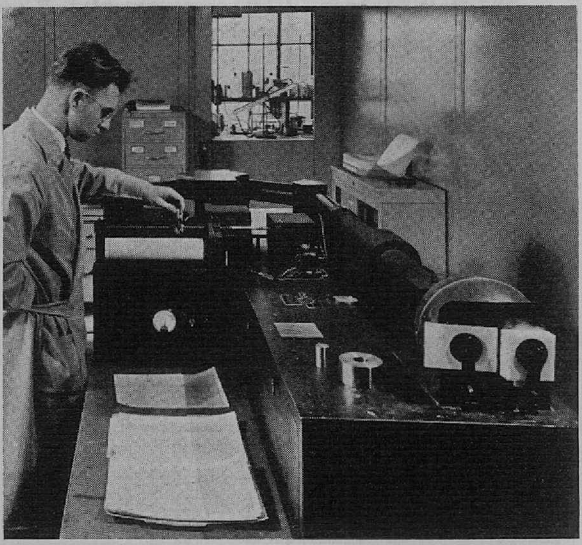
monochromatic light and the use of a fast spectrograph for photographing the scattered light with particular precautions for the elimination of stray light reflected from the illuminated vessel. The illumination vessels have taken a great variety of forms (*100*).

A typical vessel consists of a cylindrical tube provided with a plane optically flat window at one end, with the other end of the tube drawn out into a bent horn, which is blackened to minimize reflection. The sample tube is usually surrounded with a cooling jacket and highly selective filters are used to isolate the exciting line from a suitable source, usually a mercury arc. Numerous arrangements have been suggested to provide an efficient "light-furnace", so that the sample may be submitted to the highest possible amount of lateral illumination. The spectrograph is sighted on a portion of the sample in such a manner that the maximum amount of scattered light may be collected, yet avoiding all direct reflection from the source.

APPLICATIONS. The qualitative identification of substances is comparatively simple and amounts to accurate determination of the frequencies of the Raman lines which appear on the spectrogram. The Raman frequencies for an enormous amount of compounds have been recorded (*128*) and reference to these tables permits identification of the substance. In general, the sensitivity of the method is much less than one ordinarily associates with other spectroscopic methods, which is largely due to the feeble intensities characteristic of the Raman effect. In most cases a substance present to the extent of about 1 per cent can be detected, but under

FIGURE 63. DOUBLE MONOCHROMETER SPECTROPHOTOMETER IN CHEMICAL RESEARCH

Courtesy, Coleman Electric Co. and Armour and Co.



Courtesy, Interchemical Corp.

FIGURE 64. GENERAL ELECTRIC RECORDING SPECTROPHOTOMETER

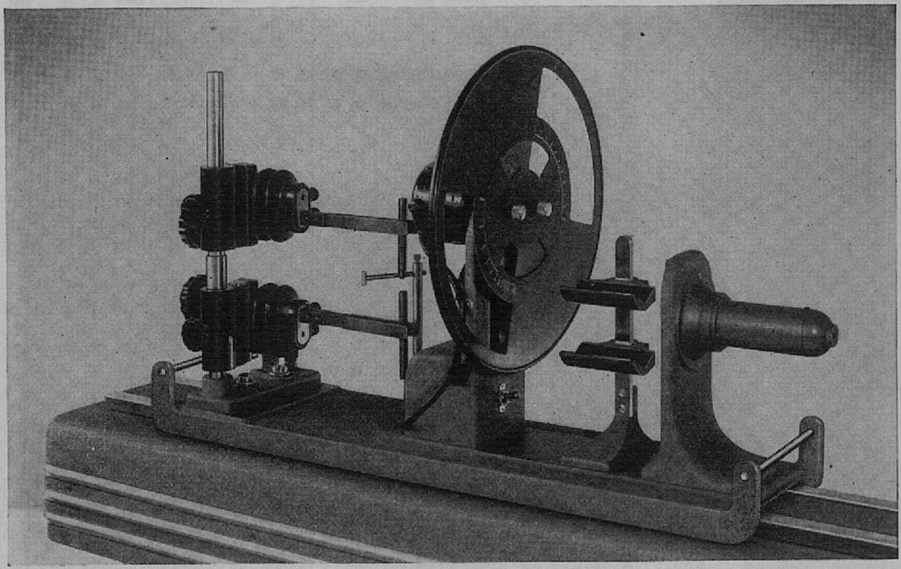


FIGURE 65 (*Left*). ROTATING SECTOR

Courtesy, Bausch & Lomb Optical Co.

favorable circumstances to 0.1 per cent. A few examples from Goubeau (*100*) illustrate this point. The detectable limits were found to be 1 to 2 per cent for benzene in dioxane or *vice versa;* 1 per cent for *trans*-crotonaldehyde in *cis*-crotonaldehyde; 0.5 per cent for *p*-xylol in *m*- or *o*-xylol; 0.1 per cent for benzene in carbon tetrachloride.

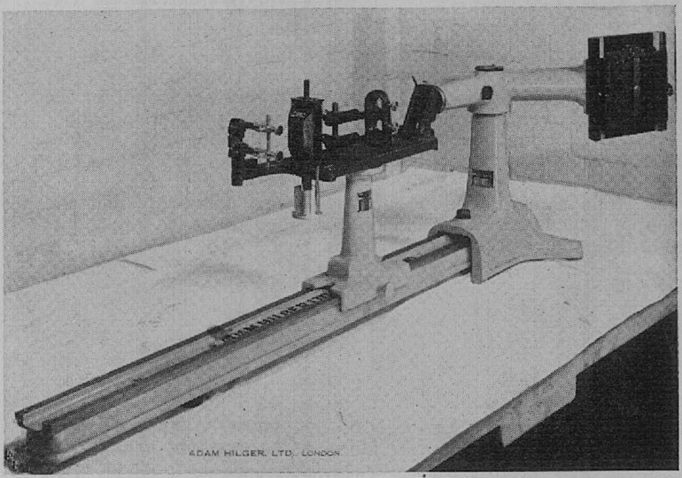
Quantitative analyses based on the Raman effect are feasible, but these involve all the usual difficulties associated with photographic photometry. Theoretically mixtures of several substances can be analyzed, but the number of Raman lines increases very rapidly with the number of components in the mixture. Certain other complications arise with respect to both the intensity and the frequency, if the system is one in which molecular interaction can arise. Procedures have been developed (*47*, *100*) utilizing a technique similar to the Gerlach principle of homologous pairs of lines and comparing their relative intensities. By calibration with mixtures of known composition very satisfactory results can be obtained with a precision of ±10 per cent without the use of a microphotometer. With the full resources of microphotometry and the usual plate calibration, somewhat more precise evaluation can be made. For further details the reader is referred to Goubeau (*100*), who lists 97 references, most of them concerned with analytical applications. Specific examples are also given by Cringler (*47*) and Hibben (*128*).

X-Rays

The analytical uses of x-rays comprise a very small fraction of all contributions which this subject has made to physical science. Their use in medical radiography, inspection of materials, the elucidation of structure of crystals, etc., is well known and has been set forth in many treatises (*39*, *50*, *122*, *187*, *241*, *254*, *305*), which also discuss analytical uses. Some of the distinctly analytical uses may be listed as shown on the next page.

FIGURE 66 (*Below*). SPEKKER PHOTOMETER WITH SMALL QUARTZ SPECTROGRAPH

Courtesy, Jarrell-Ash Co. and Adam Hilger, Ltd.



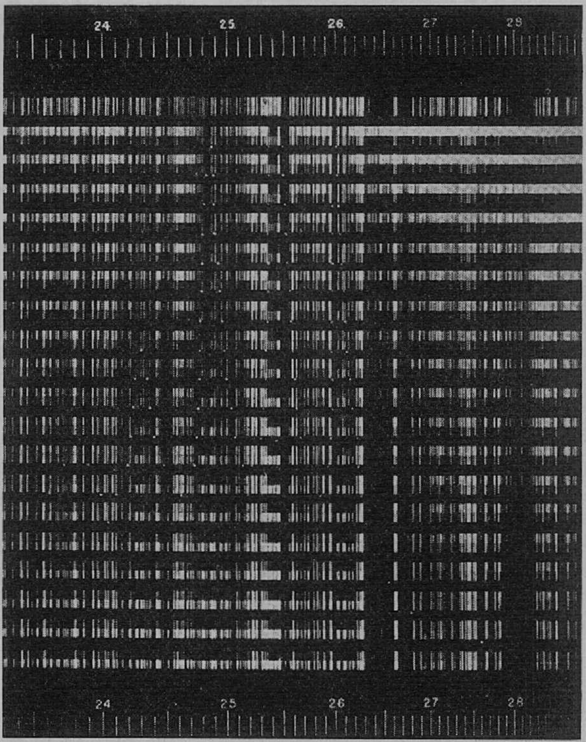
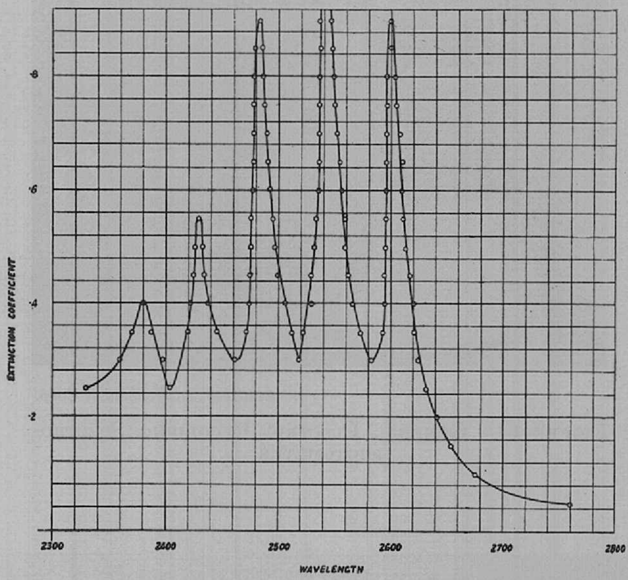


FIGURE 67 (*Left*). ABSORPTION PHOTOGRAPH OF BENZENE (IN HEXANE)

Taken with Spekker ultraviolet photometer and medium all-metal quartz spectrograph. Length of tube 2.0 cm. Minimum exposure 5 seconds

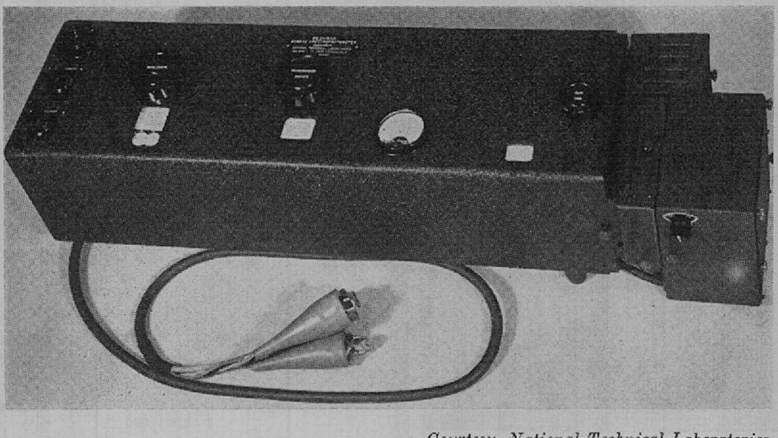
Courtesy, Jarrell-Ash Co. and Adam Hilger, Ltd.



Courtesy, Jarrell-Ash Co. and Adam Hilger, Ltd.

FIGURE 68. ABSORPTION CURVE OF BENZENE (IN HEXANE)

Strength of solution, 1 in 3300



Courtesy, National Technical Laboratories

FIGURE 69. BECKMAN PHOTOELECTRIC QUARTZ SPECTROPHOTOMETER

1. Measuring the spectral emission lines (*K*, *L*, *M*, series) in which the unknown substance is the target of an x-ray tube. This method on the basis of Moseley's law has accounted for the original discovery of a number of the elements (Hf, Ma, Re).
2. Measurement of the secondary fluorescence lines emitted by the substance when it is irradiated by x-rays inside the x-ray tube (*14*).
3. The same technique of fluorescence emission with the sample placed outside the x-ray tube, identical with No. 2 but affording somewhat lower intensities.
4. Measuring the wave lengths of the characteristic absorption edges when the unknown substances act as the absorbing medium.
5. Determination of the lattice constants of the material, from which the nature of the substance may be inferred, and from the intensity of the lines of the pattern its amount may be inferred.

The possibility of identification presupposes that the lattice constants characteristic of that substance have already been determined—that is, it is impossible to infer the nature of the substance if no values have been recorded for its lattice parameters.

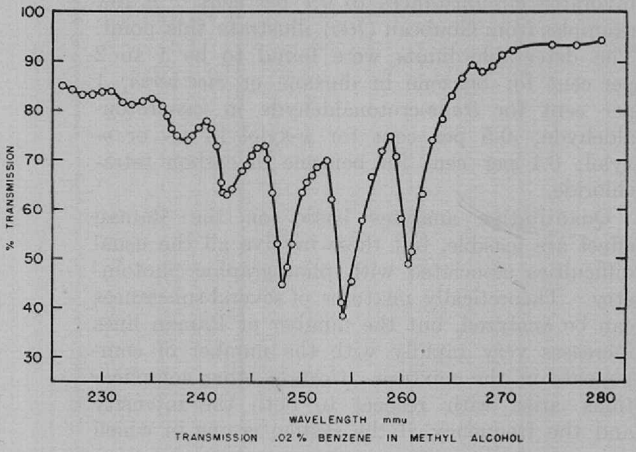


FIGURE 70 (*Right*). ABSORPTION SPECTRUM MEASURED WITH BECKMAN PHOTOELECTRIC QUARTZ SPECTROPHOTOMETER

Courtesy, National Technical Laboratories

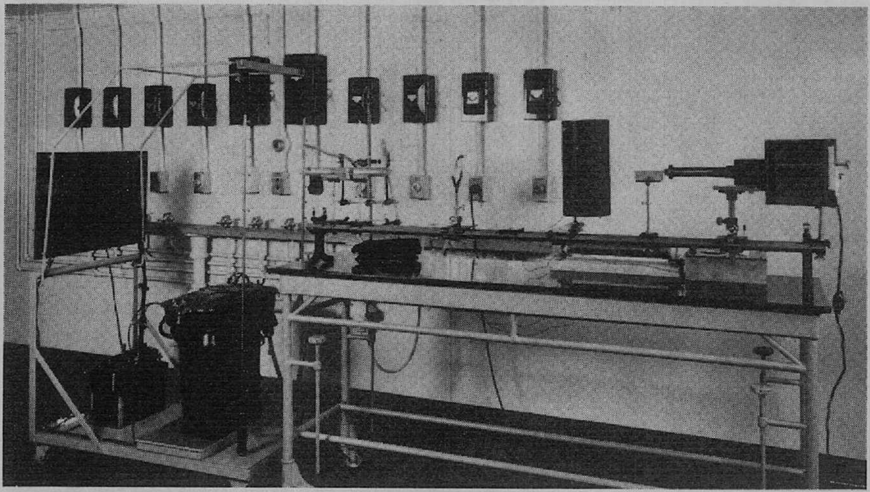


FIGURE 71 (*Left*). INSTALLATION FOR ULTRAVIOLET ABSORPTION SPECTRA

Using quartz hydrogen discharge tube and small Hilger spectrograph

Courtesy, G. I. Lavin, Rockefeller Institute for Medical Research

THEORY. The interplanar distance is given by Bragg's law

$$n\lambda = 2d \sin \theta$$

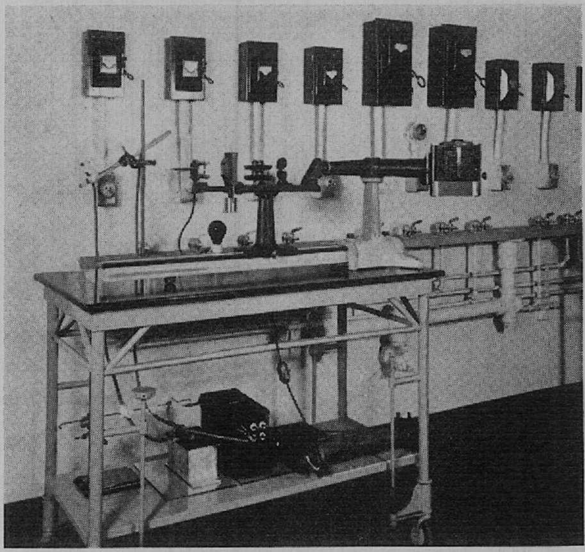
This is the fundamental law for the analysis of structure of crystal in substances. Very slight departures from this law are due to refraction, but these corrections are known and have to be applied only for high orders of reflection.

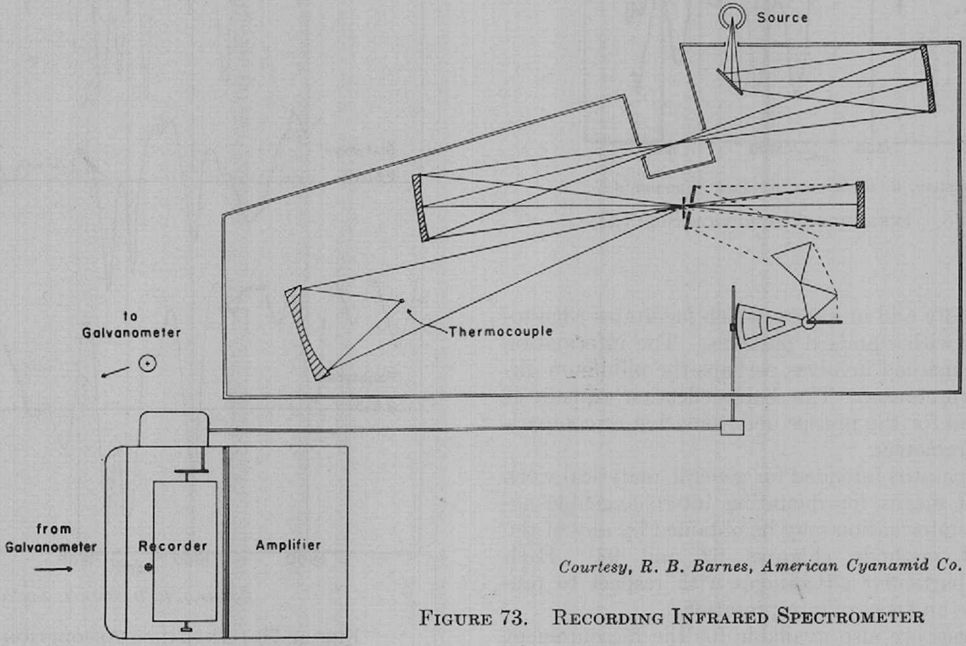
The theory of various space groups and the interpretation for crystals of various classes are the subject of exhaustive treatment in many standard tests.

INSTRUMENTS AND METHODS. The variety of instrumental approaches to x-ray analysis is evident in Figures 81 to 91. By exposing a substance to a narrow monochromatic beam of x-rays and recording the diffracted beam on a flat plate behind the sample (Figure 83) the familiar Laue pattern is produced (Figure 85). Interpretation of these patterns is described in detail in all the principal references. In the powder method the camera surrounds the specimen as a concentric cylinder (Figure 86) and diffraction patterns can

FIGURE 72 (*Below*). INSTALLATION OF SPEKKER SPECTROPHOTOMETER (HILGER)

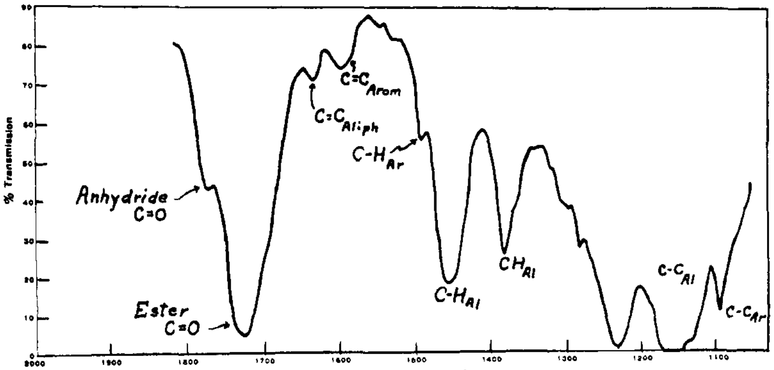
Courtesy, G. I. Lavin, Rockefeller Institute for Medical Research





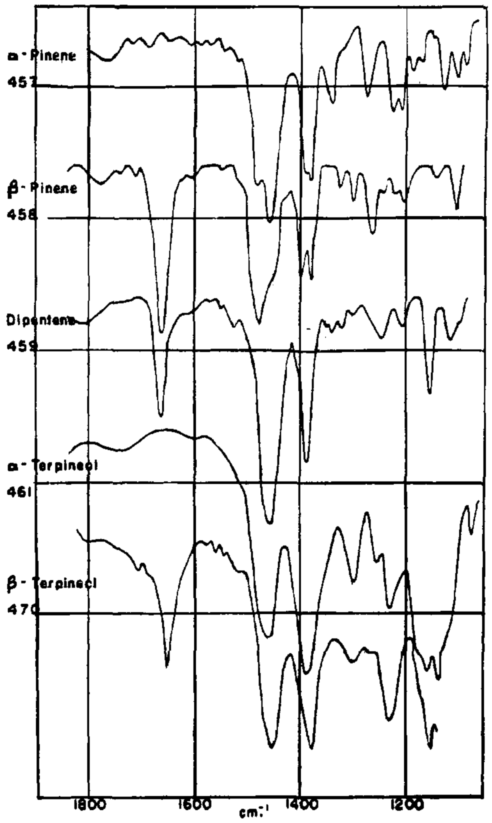
Courtesy, R. B. Barnes, American Cyanamid Co.

FIGURE 73. RECORDING INFRARED SPECTROMETER



Courtesy, R. B. Barnes, American Cyanamid Co.

FIGURE 74. INFRARED ABSORPTION SPECTRUM OF A RESIN, WITH IDENTIFICATION OF BAND HEADS



Courtesy, R. B. Barnes, American Cyanamid Co.

FIGURE 75. INFRARED ABSORPTION SPECTRA

be registered rapidly and in a form which facilitates edge-to-edge comparison with standard patterns. The information obtained by this method involves perhaps the minimum difficulties of interpretation. The back-reflection camera is particularly suited for the precise determination or comparison of lattice parameters.

Most x-ray apparatus intended for general analytical work is provided with means for mounting interchangeable accessories, so that information may be obtained by any of the above-mentioned methods (Figures 92 and 93). Each method has its particular advantages with respect to precision, sensitivity, and ease of interpretation.

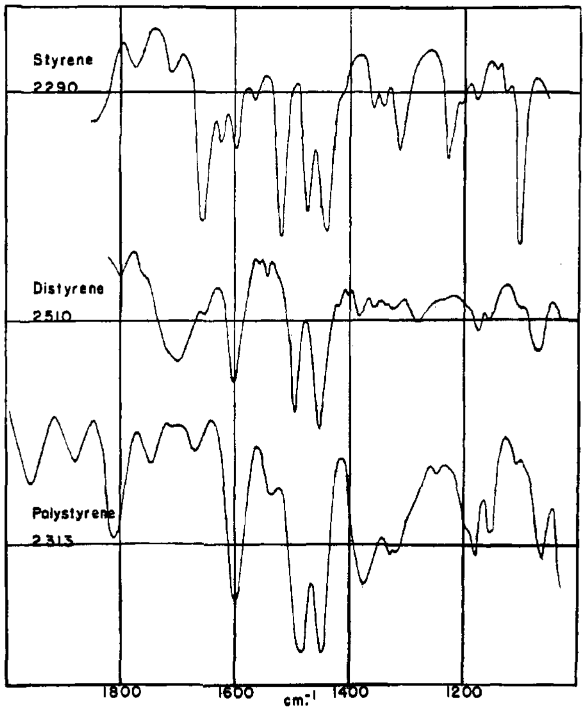
Many accessories are also available for the measurement and rapid evaluation of the patterns (Figure 94). Full details are given by Clark (*39*). No mention is made here of x-ray spectrometers of extraordinarily high precision, such as the double crystal spectrometer. These are available but are intended primarily for fundamental research on lattice constants or conversely for studies on the fine structure of x-ray lines. The analyst is not concerned with their use, although he is always appreciative of the exact information which they can provide.

APPLICATIONS. A list of applications is to be found in monographs and in several interesting papers, such as (*1*).

A recent compilation by Hanawalt (*107*) lists over 1000 substances in terms of the three strongest lines on the diffraction pattern with the respective interplanar distances. The efficiency and convenience of their index are amply demonstrated and it is shown that if the unknown substance is identical with one of the 1000 its presence may be certified in a few minutes by reference to the catalog.

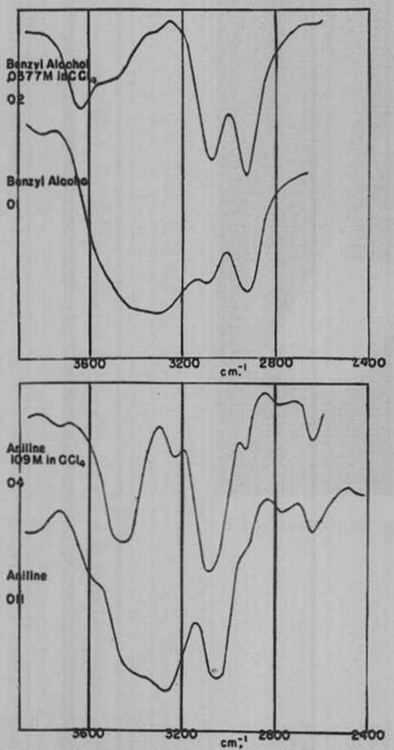
One distinctive feature of the x-ray method, and one which should be kept in mind in comparing it with alternative methods of analysis, is the fact that it identifies compounds. In other words, if one is dealing with a system containing sodium, potassium, chlorine, and bromine, it is possible to tell whether one is dealing with sodium chloride and potassium bromide or sodium bromide and potassium chloride.

The many applications of these methods to analytical problems are the object of an extended review which is now being prepared.



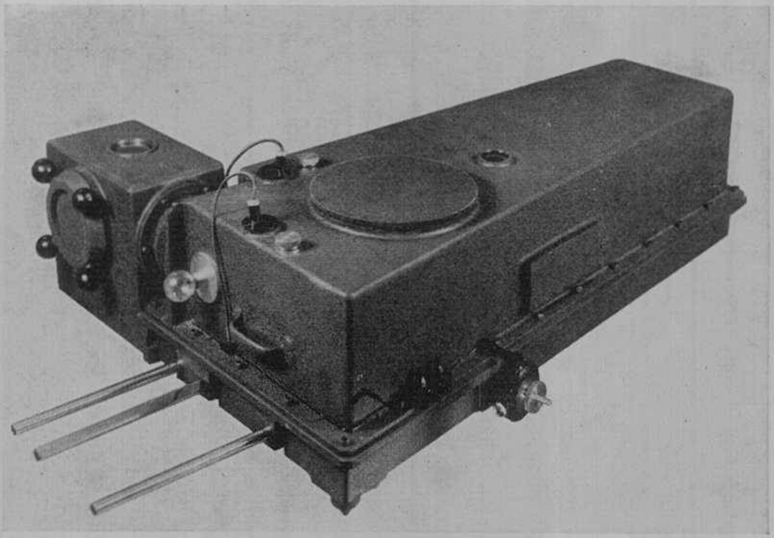
Courtesy, R. B. Barnes, American Cyanamid Co.

FIGURE 76. INFRARED ABSORPTION SPECTRA



Courtesy, R. B. Barnes, American Cyanamid Co.

FIGURE 77. INFRARED ABSORPTION SPECTRA



Courtesy, Gaertner Scientific Corp.

FIGURE 78. LARGE INFRARED SPECTROGRAPH

Electron Diffraction

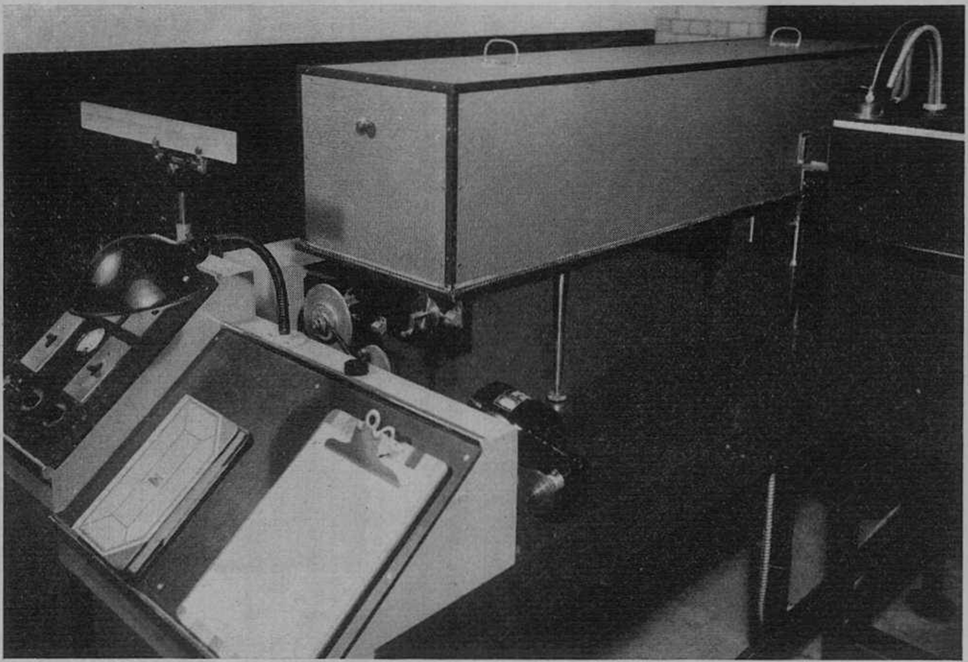
The wave nature of the electron is expressed by the de Broglie equation

$$\lambda = h/mv$$

where λ is the wave length, m and v are the mass and velocity of the electron, respectively, and h is Planck's constant. The numerical value in Ångström units is given by

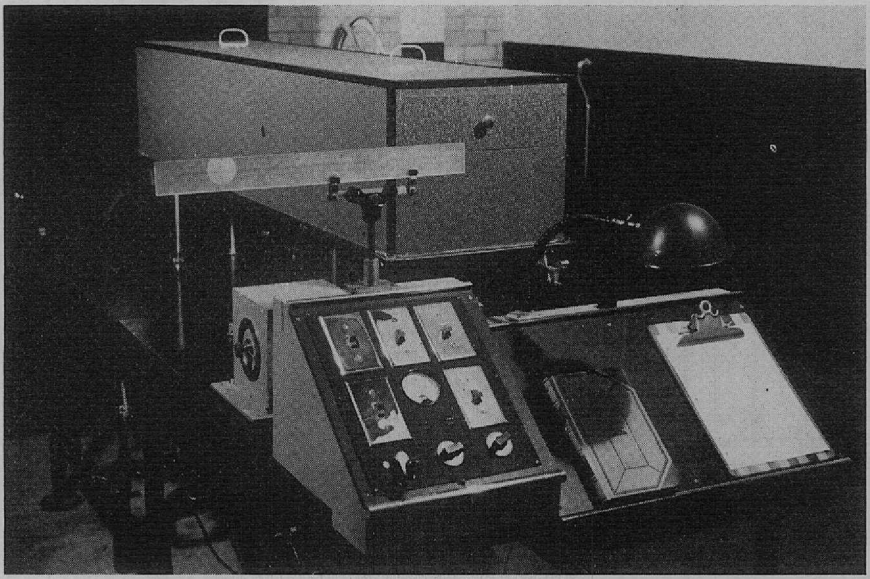
$$\lambda_{\text{Å.}} = \sqrt{\frac{150}{V}}$$

where V is in volts.



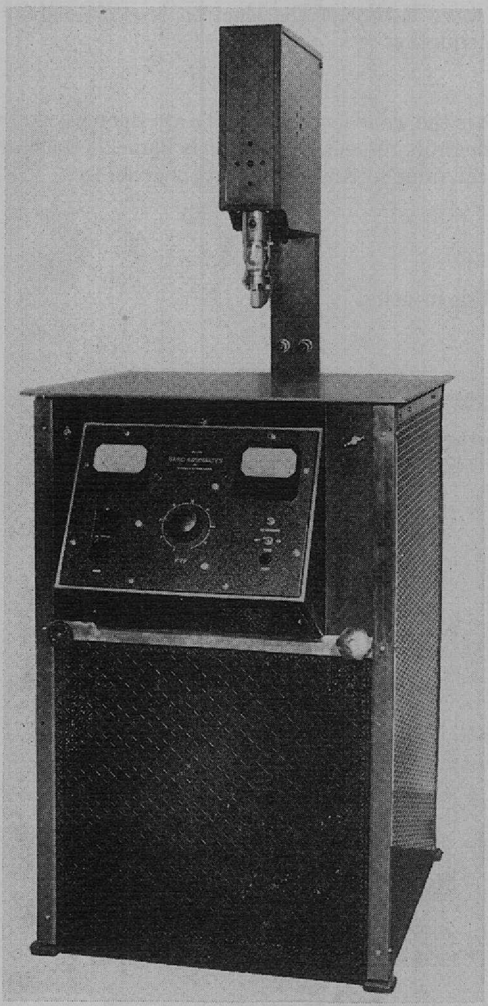
Courtesy, Dow Chemical Co.

FIGURE 79. RECORDING INFRARED SPECTROGRAPH



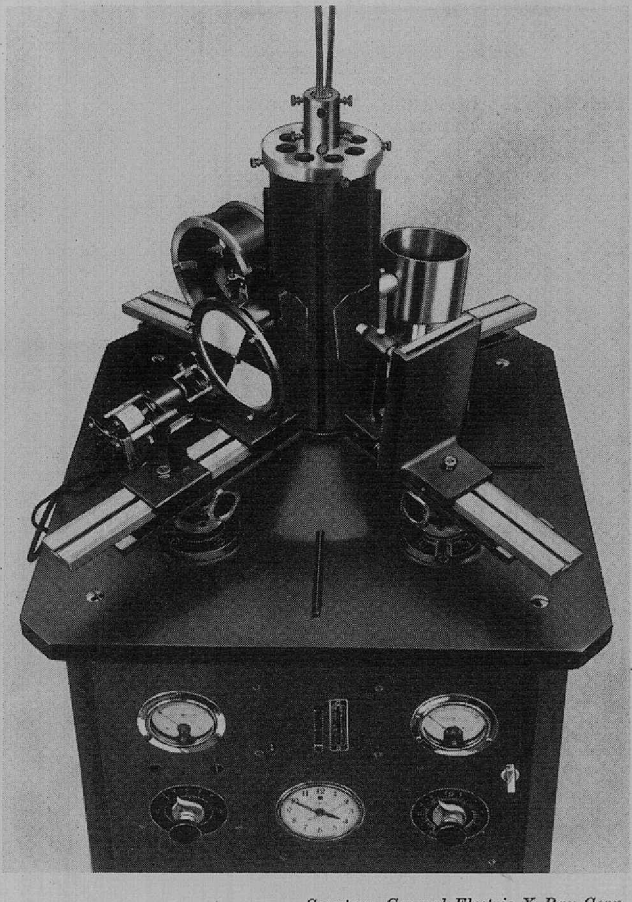
Courtesy, Dow Chemical Co.

FIGURE 80. RECORDING INFRARED SPECTROGRAPH



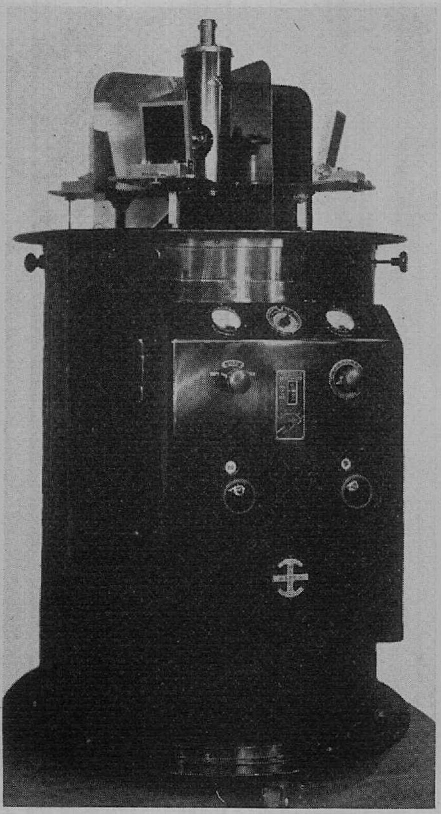
Courtesy, Baird Associates

FIGURE 81. X-RAY DIFFRACTION UNIT FOR RESEARCH



Courtesy, General Electric X-Ray Corp.

FIGURE 82. IN CLOCKWISE ORDER, STARTING AT UPPER LEFT, XRD CYLINDRICAL POWDER CAMERA, BACK-REFLECTION CAMERA, PINHOLE ASSEMBLY AND FLAT CASSETTE, AND UNIVERSAL SPECIMEN MOUNT WITH CYLINDRICAL CASSETTE MOUNTED ON X-RAY DIFFRACTION UNIT



Courtesy, G. L. Clark, University of Illinois

Figure 83. Multiple X-Ray Diffraction Unit (Hayes)

Designed at University of Illinois for photographing four patterns simultaneously

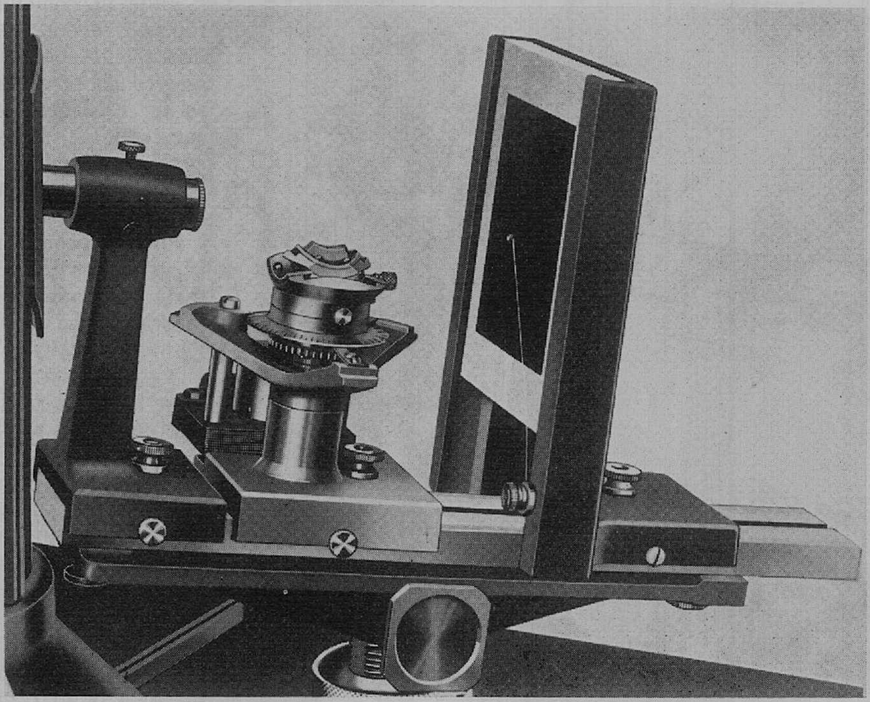
The work of G. P. Thomson, Davisson and Germer, and Rupp has shown that lattice constants may be interpreted from electron diffraction patterns in a fashion analogous to that of x-rays. The technique is primarily suited to films which are thin enough to be penetrated by the electron beams, or to surface films from which they may be reflected. The extension of this method to gases and vapors has been reviewed by Brockway (*29A*).

A typical analytical application is illustrated by the electron-diffraction apparatus of the Dow Chemical Company (Figures 96 and 97), a hot-filament tube operated at $-45,000 \pm 3$ volts. The accelerated electrons pass through a 0.2-mm. pinhole in a copper target and are then focused by a magnetic lens before they impinge on the specimen (the adjustable specimen holder accommodates three samples). The pattern made by the diffracted electrons is then recorded on a photographic plate, 18 × 6 cm. A hexagonal drum in the camera proper carries five plates and a fluorescent screen. The specimen-to-plate distance of the apparatus is 75 cm. Two oil diffusion pumps serve to maintain a vacuum of 10^{-5} mm. of mercury in the entire system. The apparatus was designed and set up by L. K. Frevel and L. Sturkey and has been used primarily in the identification of surface coatings.

Figure 98 reproduces the reflection patterns of magnesium oxide and magnesium hydroxide.

Photometric

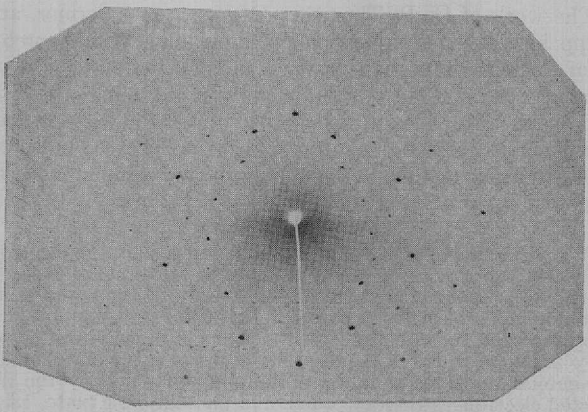
A photometer serves for the comparison of light intensities, which may be from different sources, or from a common source, one portion of the light having been reduced in intensity as a result of absorption or reflection losses. Heterochromatic photometry is of little use in chemical investigations; its use is confined to the measurement and evaluation of illuminants. For all colored substances, it is necessary to restrict the radiation to a narrow region of the spectrum.



Courtesy, General Electric X-Ray Corp.

Figure 84. XRD Universal Specimen Mount with Pinhole Assembly and Flat Cassette

For orientation and estimation of degree of internal strain in a single crystal



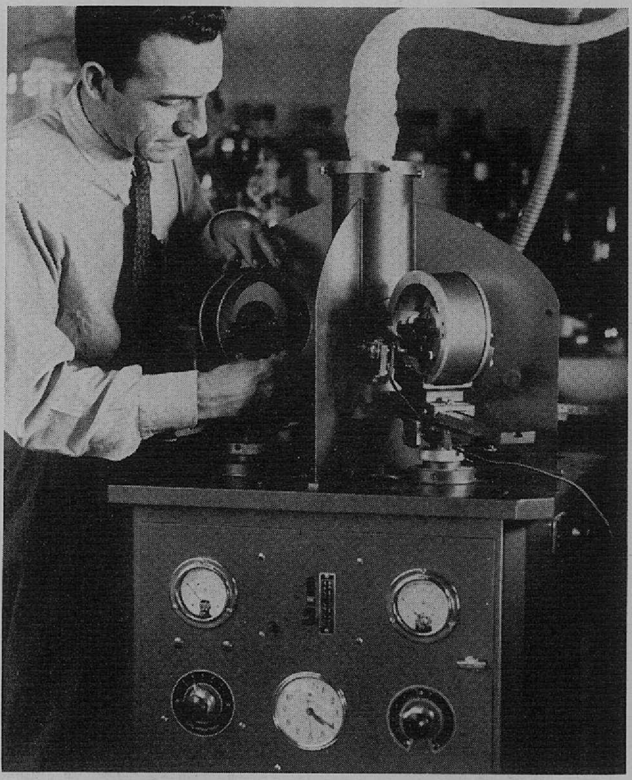
Courtesy, General Electric X-Ray Corp.

FIGURE 85. SLIGHTLY ASYMMETRIC LAUE PATTERN

Obtained from a single sodium chloride crystal, oriented so that x-ray beam is $20 \pm 2'$ from perpendicular to the [001] direction and $2^\circ 40 \pm 2'$ from parallel to the [110] direction

This is usually achieved by the use of filters and the instrument is then designated as a filter photometer. In principle it resembles a spectrophotometer, but since the isolation of the spectral region with a filter produces a wider band than dispersion by a monochromator and offers a smaller choice of spectral regions, the instrument is often called an abridged spectrophotometer.

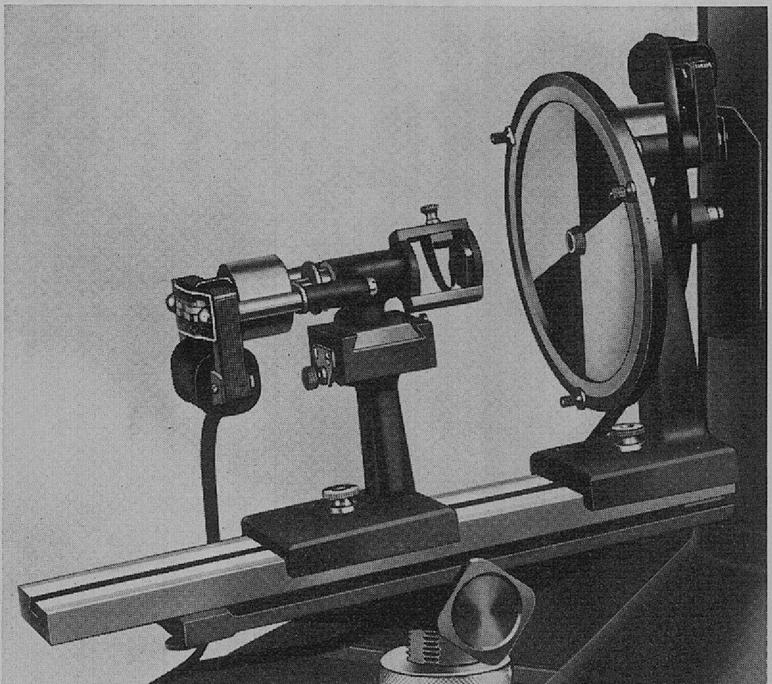
An exception to this point may be made if, for example, a discontinuous source of radiation is used (mercury arc) supplemented by a highly selective filter; it is then possible to isolate a single line and the photometric comparison need not be inferior to that of a spectrophotometer.



Courtesy, Thomas & Hochwalt Laboratories Division, Monsanto Chemical Co.

FIGURE 86. POWDER CAMERA OF X-RAY DIFFRACTION UNIT

Dexter H. Reynolds adjusting powder camera of G-E x-ray diffraction unit. Provision is made for recording diffraction patterns from all types of samples in powder of polycrystalline block form. Diffraction patterns are registered rapidly, and are of a form to facilitate edge-to-edge comparison with standard patterns.



Courtesy, General Electric X-Ray Corp.

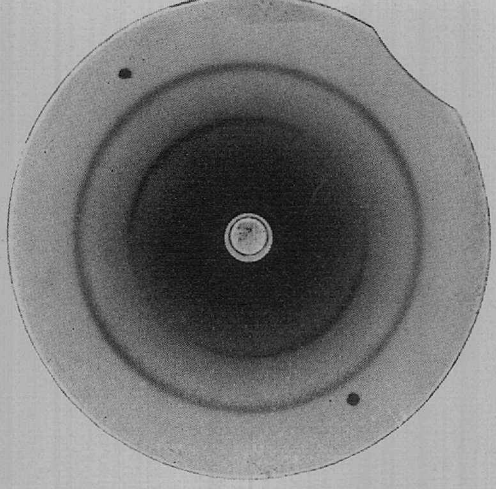
FIGURE 87. BACK-REFLECTION CAMERA

XRD camera with 60° window cassette shield in position. Shield permits consecutive registration of three patterns on same film for comparison.

Filter photometers are extremely useful and several commercially available instruments can be had with a large assortment of accessories enabling them to be used for related measurements such as gloss, reflection, albedo, fluorescence, turbidity, and as trichromatic colorimeters, or as comparison microscopes.

Filter photometers are of two general types—those in which the photometric match is made with the eye and those in which the measurement is effected photoelectrically. The assumption that any photoelectric instrument must be more accurate and reliable than a visual instrument is wholly unwarranted. A very critical and authoritative appraisal of this point has been given by Gibson (*197*). However, the future does seem to lie in the direction of the photoelectric types, for there is no inherent limit in the attainable sensitivity and objectivity of the measurement. Fatigue effects again incline toward the photoelectric type, although squinting at a microammeter needle for protracted periods is not a pleasant pastime.

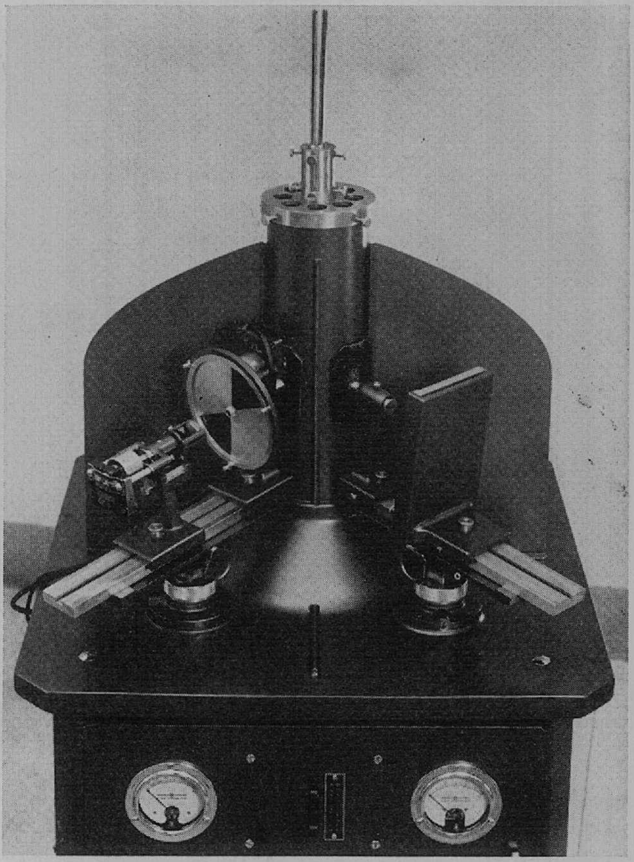
The relative uses and merits of the filter photometer and spectro-



Courtesy, General Electric X-Ray Corp.

FIGURE 88. BACK-REFLECTION PATTERN OF COLD-ROLLED TEMPERED BRASS STRIP TAKEN WITH SHIELD REMOVED

Variation in intensity around inner diffraction ring permits determination of degree of preferred orientation or texturing induced by cold rolling. Width of diffraction lines is measure of degree of internal strain, a property which determines variations in hardness and strength of polygrained metals.



Courtesy, G. L. Clark, University of Illinois and General Electric X-Ray Corp.

FIGURE 89. XRD UNIT WITH X-RAY TUBE AND CAMERAS

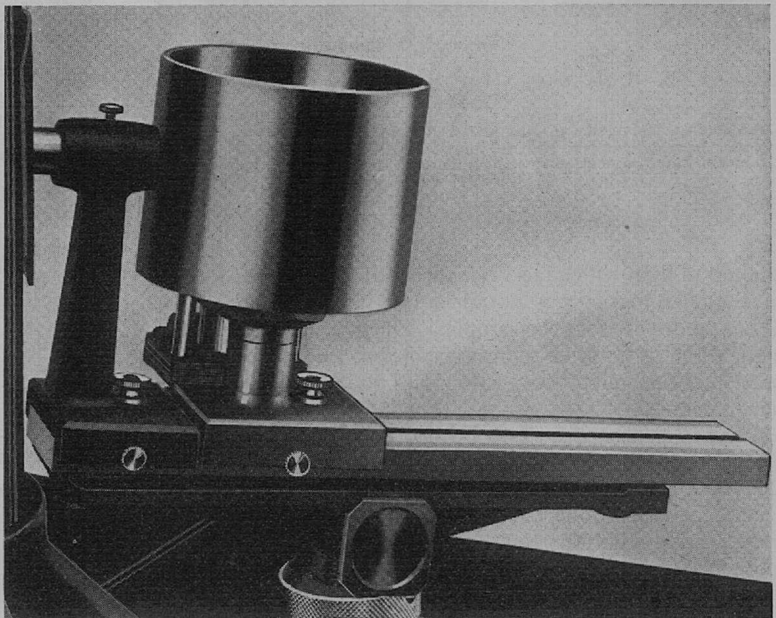
Showing back-reflection camera (*left*) and flat cassette for very accurate measurement of line shifts in solid solutions, etc. (*right*)

photometer must also be approached with common sense, whether one is dealing with the visual or photoelectric type. It is largely the change in extinction with wave length that is important. The photometric matching is equally reliable for the two classes of instrument. In other words, if the substance to be measured possesses very sharp absorption bands, such as hemoglobin or a neodymium salt, a spectrophotometer may be used in any region of the spectrum, but a filter photometer would be restricted to some region not occupied by sharp bands, and therefore probably to one which is very insensitive to small changes in concentration. The error is never unconsciously made (with a visual instrument), however, since the failure of a filter instrument due to such causes is at once apparent—i. e., it is difficult to secure two fields of the same hue.

For those problems in which the absorption bands are broad, and this includes hundreds of important systems, there is little choice between the two, and the less expensive instrument is to be preferred.

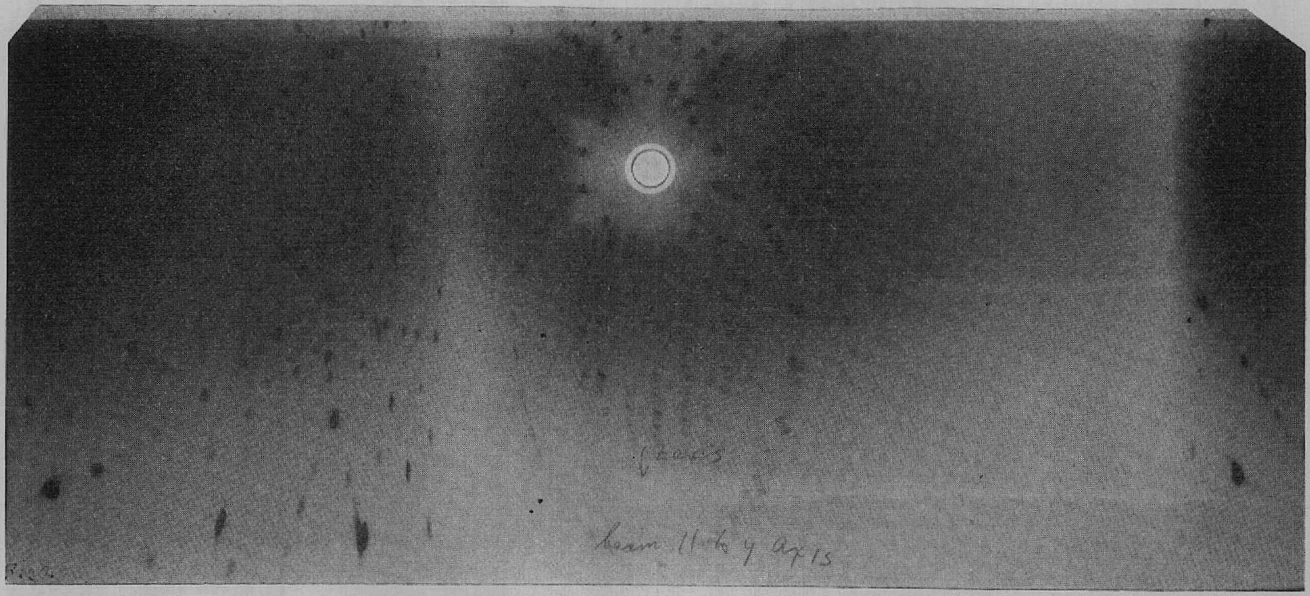
In the measurement of mixtures, the filter photometer is likely to impose empirical calibration, whereas the spectrophotometer can be depended upon to yield additive extinction values. There are other considerations applying to mixtures—i. e., the relative values of the separate extinction coefficients which limit the accuracy (*114*).

THEORY. A filter photometer consists of a light source, an appropriate optical system for producing a parallel beam of light, a container for the light-absorbing sample, or means for reflection from the sample, and means for measuring the



Courtesy, General Electric X-Ray Corp.

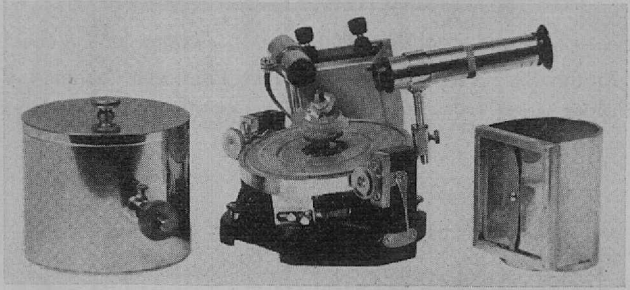
FIGURE 90. UNIVERSAL SPECIMEN MOUNT IN USE WITH CYLINDRICAL CASSETTE



Courtesy, General Electric X-Ray Corp.

FIGURE 91. PATTERN OBTAINED IN CYLINDRICAL CASSETTE MOUNTED ON UNIVERSAL SPECIMEN MOUNT

Records pattern of a stationary quartz oscillator orientated so that x-ray beam coincides approximately with electric axis of crystal and central axis of cassette coincides with optical axis of cassette. Faces of oscillator contain optical axis and make acute angle with electric axis. Characteristic piezoelectric frequency of an oscillator may be predetermined by specifying relation between its physical dimensions and crystallographic axes. Piezoelectric properties are constant over a longer life if this relation meets exact specifications. Routine determination of orientation of crystallographic axes in rough quartz crystals by x-ray diffraction techniques is standard practice with large manufacturers of quartz oscillators.



Courtesy, G. L. Clark, University of Illinois

FIGURE 92. UNIVERSAL CAMERA FOR X-RAY DIFFRACTION (HAYES)

Designed at University of Illinois. *Left*, powder and rotation camera. *Center*, base of camera and goniometer mounting for single crystal (Laue or rotation method). *Right*, mounting of flat film for Laue or fiber pattern.

amount of light which has been absorbed. An approximation to monochromaticity is obtained by suitable filters, placed either before or after the sample. The measurement may be made directly (in some photoelectric instruments) or by comparison with a reference beam (visual and some photoelectric instruments).

Visual Instruments. Two beams of light from a common source, one passing through or reflected from the sample, the other passing through some device which reduces its intensity in measurable amount, are brought together as adjacent fields and are compared with an eyepiece. Three methods for weakening the comparison beam are commonly employed:

1. Aperture type in which a slit or diaphragm is opened or closed. The intensity is a function of the aperture and in the case of a square aperture moving along a diagonal (Zeiss) follows a square law.

$$I = k\theta^2$$

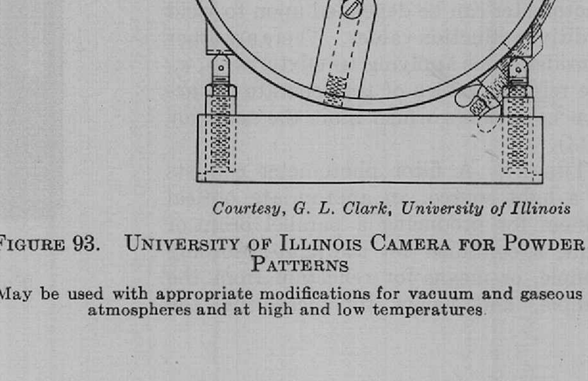
where θ is the angular motion of the feed screw

2. Polarization type in which the comparison beam is rendered plane-polarized and reduced in intensity by a rotatable analyzer. The intensity variation follows the law

$$I = I_0 \cos^2 \theta$$

Tables are usually provided with this class of instrument relating the observed angles to the corresponding transmission, density, or extinction values.

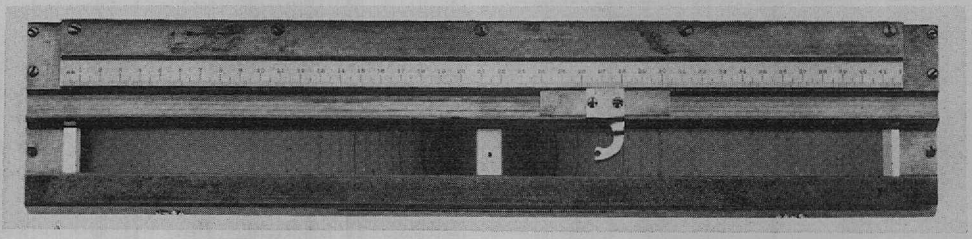
3. Neutral wedge type in which the comparison beam passes through a light-absorbing wedge. The wedge may be moved



Courtesy, G. L. Clark, University of Illinois

FIGURE 93. UNIVERSITY OF ILLINOIS CAMERA FOR POWDER PATTERNS

May be used with appropriate modifications for vacuum and gaseous atmospheres and at high and low temperatures.



Courtesy, General Electric X-Ray Corp.

Figure 94. Film Scale

XRD film scale, holding two superimposed powder camera patterns in position for measuring angles between corresponding diffraction maxima. Parameters characteristic of crystal structure of unknown samples may be read from standard tables and compared with parameters of known pure substances for absolute qualitative analysis for solid phase constituents. Rough quantitative estimation may be made from relative intensities of diffraction maxima in many cases.

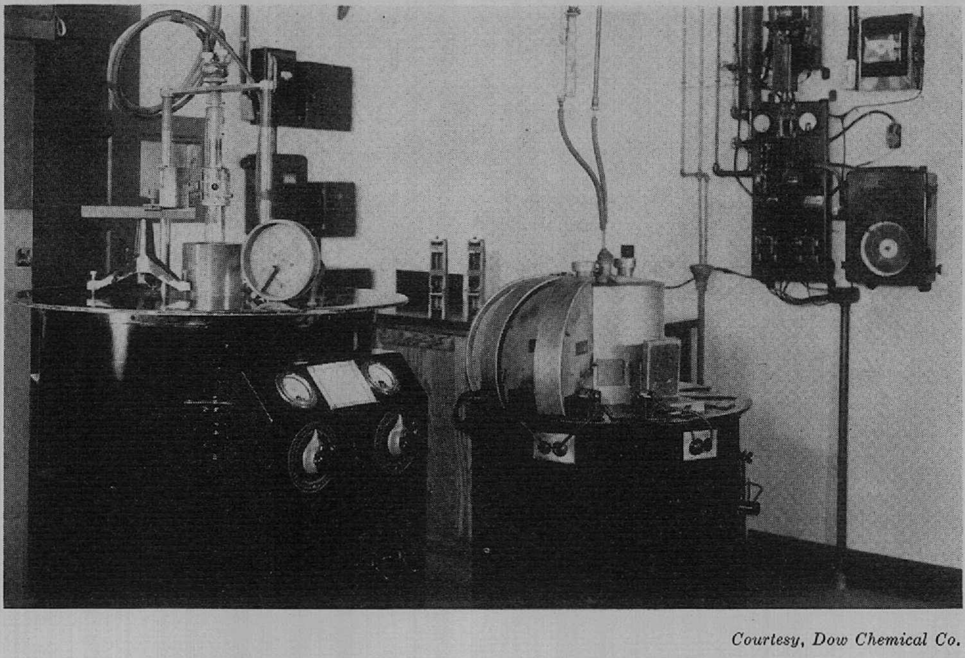
along its length, thus introducing a thinner or thicker portion. To avoid gradients in the effective portion a compensating wedge is often introduced. This is an identical wedge, turned in the opposite direction; consequently the net cross section exposed to the beam is an optically uniform rectangle. Since the intensity varies logarithmically with thickness (Lambert's law), the motion of the wedge is linear in density or extinction.

$$I \alpha - \log T \alpha d \alpha E$$

Photoelectric Instruments. There are many types and variations (*183, 213, 310*), most of which have been classified by the writer (*196*). The photocells may be of the barrier layer, emissive, or multiplier type (*197*). There are single-cell photometers with a choice of electrical methods for measuring the current—i. e., direct deflection, and potentiometric compensation of both linear and logarithmic nature (*196*). Double-cell arrangements (*299*) consist of two photocells illuminated from a common source, with the sample placed in one of the beams. Optical compensation is effected in the other beam, or the two photocurrents may be measured electrically by (*a*) opposed flow through a common meter or galvanometer, or (*b*) potentiometric or shunt cancellation. Some of these circuits compensate for source fluctuations and others do not (*196*).

Calibration and Computation of Results. Many instruments carry scales which indicate directly the measured quantity as well as derived quantities which are more directly applicable. Thus a photometer scale may read per cent transmission, density, or extinction. In others, tables are provided to translate the instrumental indication into the required information. It seems that more care, ingenuity, and real instrumentation have been practiced in the older visual instruments than in the newer photoelectric devices. Density or extinction indications are to be regarded as the ultimate goal in all photometers intended for photometric analysis.

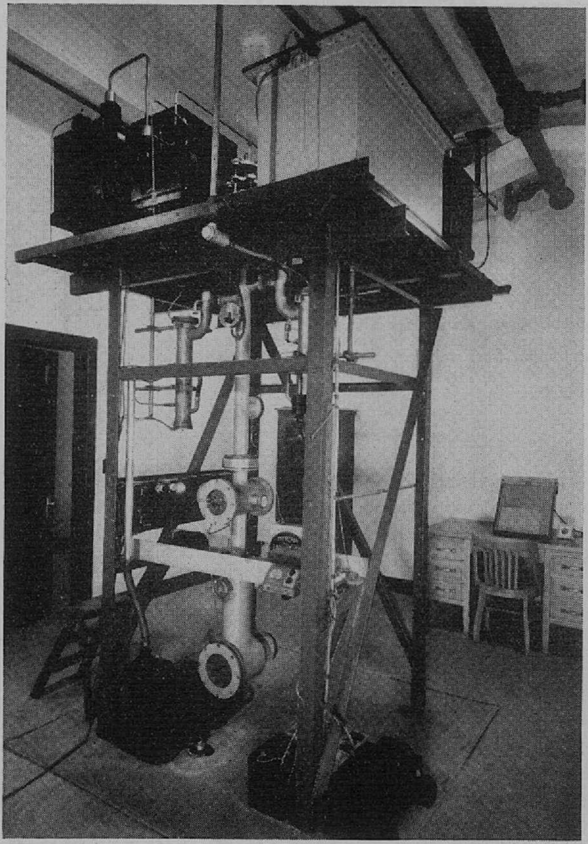
For instruments which indicate the extinction directly, the concentration is directly proportional to the reading, provided Beer's law applies. The present need for empirical calibration with known solutions in so many instances is partly due to lack of good instrumentation and also to our



Courtesy, Dow Chemical Co.

Figure 95. X-Ray Diffraction Units

Unit at right is equipped with a Mo target tube and is used mainly for routine chemical analysis by powder diffraction method. Orientation studies on metals and other substances are also made with this unit. Unit at left is equipped with a Cu target tube and is used for precision measurements of lattice parameters and for x-ray studies of polymeric substances.



Courtesy, Dow Chemical Co.

FIGURE 96. ELECTRON DIFFRACTION APPARATUS

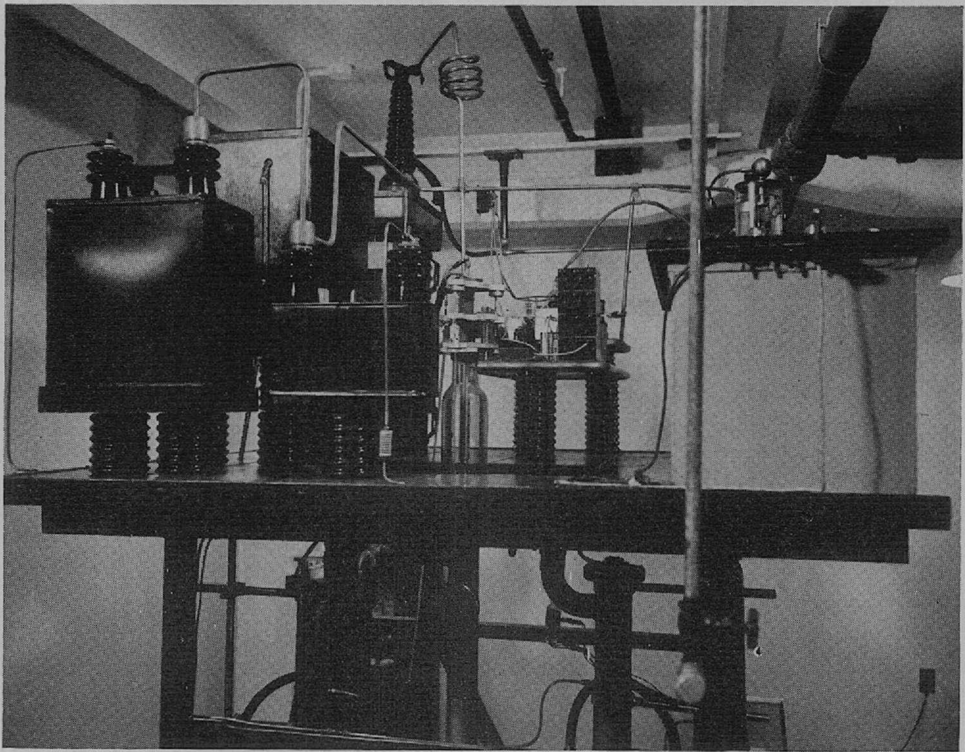
limited and still unsatisfactory knowledge of "colorimetric" chemical reactions.

An important question arises in connection with all filter photometers: To what extent can measurements reported by one investigator be duplicated by another, using a different instrument? No question of this sort arises in the use of a spectrophotometer. In some filter photometers, the photometric system is sufficiently fundamental in design and the filters are held in such rigid absolute specifications that it is possible to publish "effective extinction coefficients" for different substances with reasonable certainty that others can duplicate the results.

INSTRUMENTS. Of the many instruments available for this work we shall discuss a few which are representative of a given type or class. Some are unique in their class, others have many successful competitors.

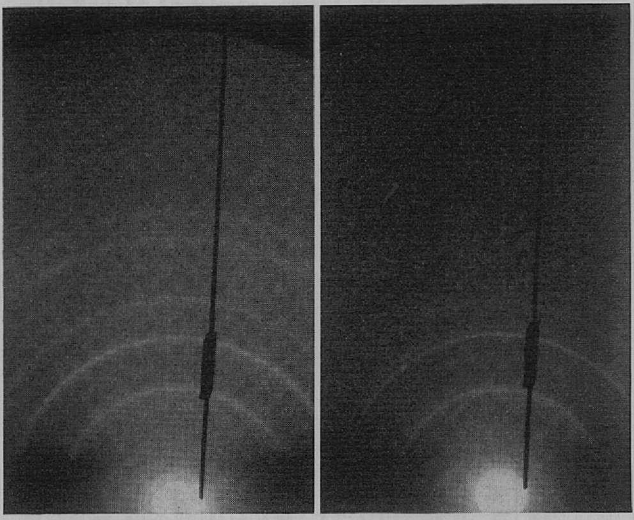
Visual Instruments. Aperture Type. The Zeiss Pulfrich photometer, shown in a general view as Figure 99 and in schematic sectional diagram as Figure 100, is a fine example of this class.

The photometer lamp contains a source, two mirrors, and two adjustable sleeves carrying focusing lenses and ground-glass diffusing screens. The photometer head carries demountable cell holders and two variable apertures which are opened or closed by rotating large measuring drums. The separate beams pass through total-reflection prisms to a biprism and the circular bipartite field is viewed with an eyepiece. A revolving filter holder permits the selection of any one of a dozen highly selective filters, which occupy a position between the biprism and the ocular. The holder normally accommodates nine filters at a time, but special filters are easily snapped in or out of the holder. The filters are extremely selective, almost opaque to normal daylight, and the spectral centers of gravity are more or less uniformly distributed throughout the visible spectrum. Complete specifications of the filters are provided by the manufacturer with respect to wave length at maximum transmission, effective center of gravity, width of band at half and



Courtesy, Dow Chemical Co.

FIGURE 97. ELECTRON DIFFRACTION APPARATUS



Courtesy, *Dow Chemical Co.*

Magnesium Oxide Magnesium Hydroxide

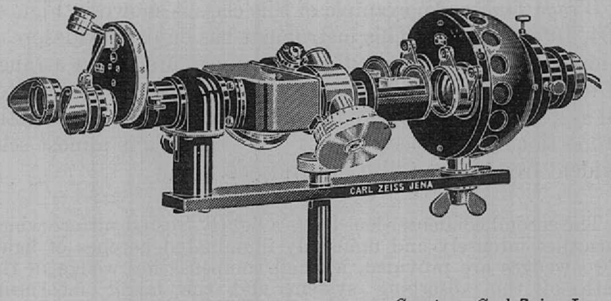
FIGURE 98. REFLECTION PATTERNS OF MAGNESIUM OXIDE AND MAGNESIUM HYDROXIDE OBTAINED WITH ELECTRON DIFFRACTION APPARATUS

tenth of maximum transmission, and transmission at the center of gravity. For example, the S61 filter (yellow) has a band width of 24 mμ at half value and 66 mμ at tenth value, a maximum transmission of 620 mμ, a center of gravity at 619 mμ, and a transmission of 0.080 per cent at this wave length. Special filters are available for use with a mercury arc source to isolate the blue line 436 mμ, the green line 546 mμ, and the yellow pair 577–579 mμ. The aperture drums are both calibrated, and read in per cent transmission and extinction. A very large assortment of accessories can be had to adapt the instrument to any type of photometric measurement. Another very convenient feature, as pointed out by Ashley (*8*) who has made extensive use of this equipment (*7*), is the ease with which absorption cells or tubes varying from a millimeter or less to 50 or more centimeters in length can be accommodated.

This instrument is worthy of the name of Pulfrich, who has contributed so much to the science of optics. Its excellence and utility are best attested by the monographs and voluminous literature devoted to its uses and applications (*114*, *285*, *285A*). Complete accessories are obtainable.

Polarization Type. An example of this class of photometer is shown in Figure 101 and in schematic view in Figure 102. This is another high-class optical instrument of perfectly general utility, which with suitable accessories can be used for every conceivable photometric problem.

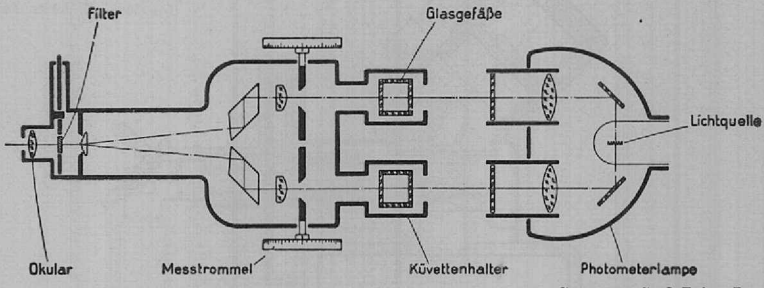
As shown in Figure 102 it is set up for the photometry of colored liquids or solutions. Light entering from the right traverses two total-reflecting prisms and rises through the adjustable absorption cell, after which it passes through a Brodhun photometer cube, through another total-reflecting prism, and out through the eyepiece and color filter. A portion of the original light beam is reflected upward on the right side of the instrument, where it is reflected from an adjustable mirror and enters the polarizing head. The second Nicol prism can be rotated to decrease the intensity and a scale indicates the angle of rotation.



Courtesy, *Carl Zeiss, Inc.*

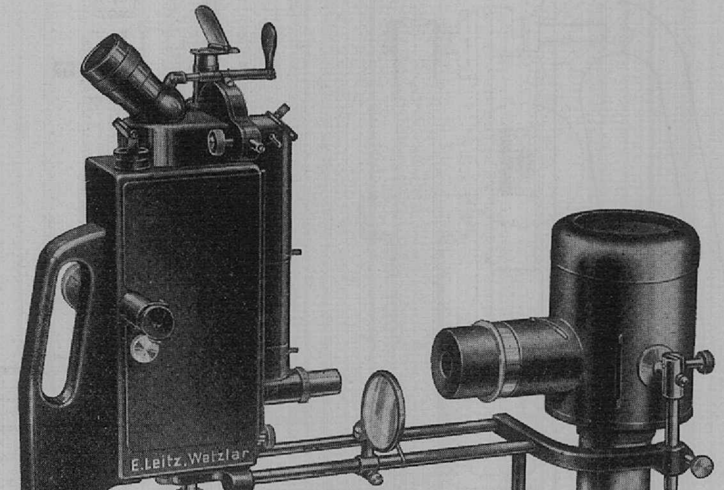
FIGURE 99. ZEISS PULFRICH PHOTOMETER

The emergent beam strikes the Brodhun photometer cube, from whence it passes through the filter and eyepiece. The photometric field appears as two semicircular patches which, upon rotation of the Nicol, can be made to merge into a single uniformly illuminated field. The computations are in terms of the general law for polarization photometers, but to save the observer's time, tables are provided relating extinction to angle of rotation of the analyzing Nicol prism. This versatile instrument has been applied to a great variety of problems (Figure 103).



Courtesy, *Carl Zeiss, Inc.*

FIGURE 100. SCHEMATIC SECTIONAL DIAGRAM OF ZEISS PULFRICH PHOTOMETER



Courtesy, *E. Leitz, Inc.*

FIGURE 101. POLARIZATION-TYPE PHOTOMETER

Wedge Type. An example of this class is shown in Figures 104, 105, and 106. This instrument has enjoyed widespread adoption and indicates extinction values directly in a range of 0 to 2.0 (100 to 1 per cent transmission), and hence for all systems obeying Beer's law the scale readings are directly proportional to concentration. The principle is almost self-evident from the detailed illustrations.

The second condenser lens bears a lightly frosted surface which furnishes intensely and uniformly illuminated patches of light. Two wedges are provided, a small compensating wedge in the path of the absorbing system and the larger measuring wedge (100 mm.). The two beams are combined as shown and pass into the eyepiece and color filter. A large selection of highly selective filters is offered, including monochromats for the blue, green, and yellow lines of the mercury arc. This company's excellent series of precision absorption cells are used with the instrument (*197*, Figure 71). The neutral wedge is practically nonselective, showing no more than 6 per cent decrease in transmission at short wave lengths and 3 per cent at long wave length. For studies at any one wave length this is of little consequence. A related instrument of the photoelectric type is discussed later.

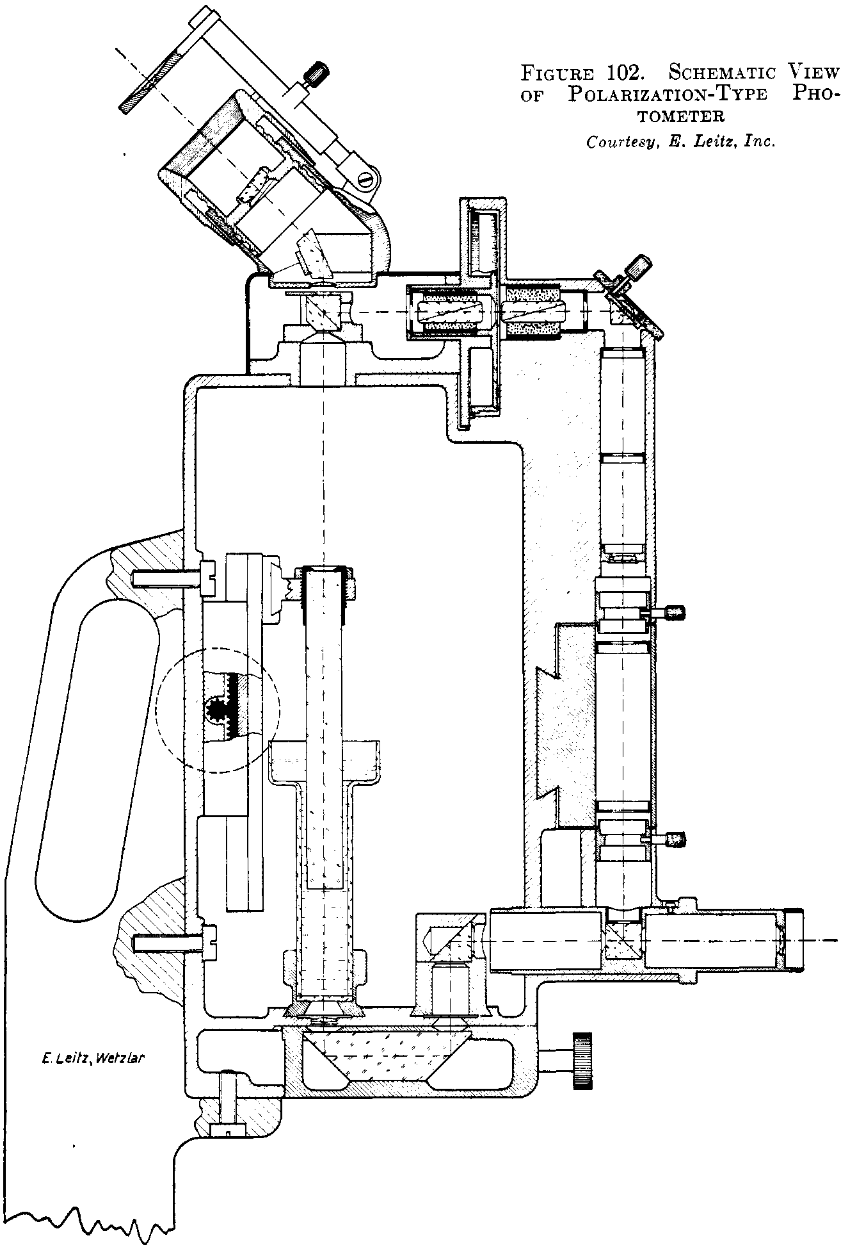


FIGURE 102. SCHEMATIC VIEW OF POLARIZATION-TYPE PHOTOMETER

Courtesy, E. Leitz, Inc.

There is little to be said in appraising the future of visual photometers. To many, their days seem to be numbered in view of photoelectric developments, but the best resources of the last half century's optical theory and practice have gone into their design and they are real instruments in a sense achieved by too few of their photoelectric successors. There is a degree of versatility, constancy, reliability, and ease with which they can be put into service at a moment's notice which is not to be ignored. As instruments they have reached the upper limit—i. e., that set by the visual acuity of the observer.

Photoelectric Photometers. A classification of these methods has been mentioned (*196*) and it may serve our purpose here to illustrate a few type examples.

Single-Cell Barrier-Layer Type. In this class, a single photocell of the self-generating type is used to measure the intensity of a semimonochromatic beam of light. Measurements are made alternately through solution and solvent and the ratio of the photocurrents indicates the transmission. Various electrical schemes other than a direct measurement of the current with a microammeter or galvanometer are used (*196*). The method requires constancy of the light source, at least during the interval in which the two readings are made. A well-known and widely used instrument of this type is shown in Figures 107 and 108.

The light source is fed from a constant-current transformer and the photocurrent is read with a Weston microammeter. The absorption cells move in a carriage in a direction perpendicular to the optic axis. A large reading glass inserted in the top of the case facilitates reading the meter. Suitable light filters are supplied, according to the location of the absorbing bands of the system.

Some compromise in selectivity of the filter is necessary with this class of instrument, since reasonably high light intensities are required. For this reason apparent deviations from Beer's law may arise which are not ascribable to the absorbing system itself. In most cases empirical calibration is recommended. These instruments are widely used in clinical work (Figure 109), as well as many other "colorimetric" analyses. A collection of methods employing this instrument has been published (*132*).

In general, the single-cell type, if it employs barrier-layer cells, must use relatively nonselective filters in order to get sufficient light or very delicate high-sensitivity galvanometers. In the latter case it is still possible to measure light resolved by a monochromator (*197*).

Single-Cell Emissive Type. The use of a phototube, usually with amplification, has not met with extensive commercial use, although many sensitive circuits have been de-

Courtesy, E. Leitz, Inc.

Figure 103. Leitz-Leifo Photometer at Metropolitan Life Insurance Co.

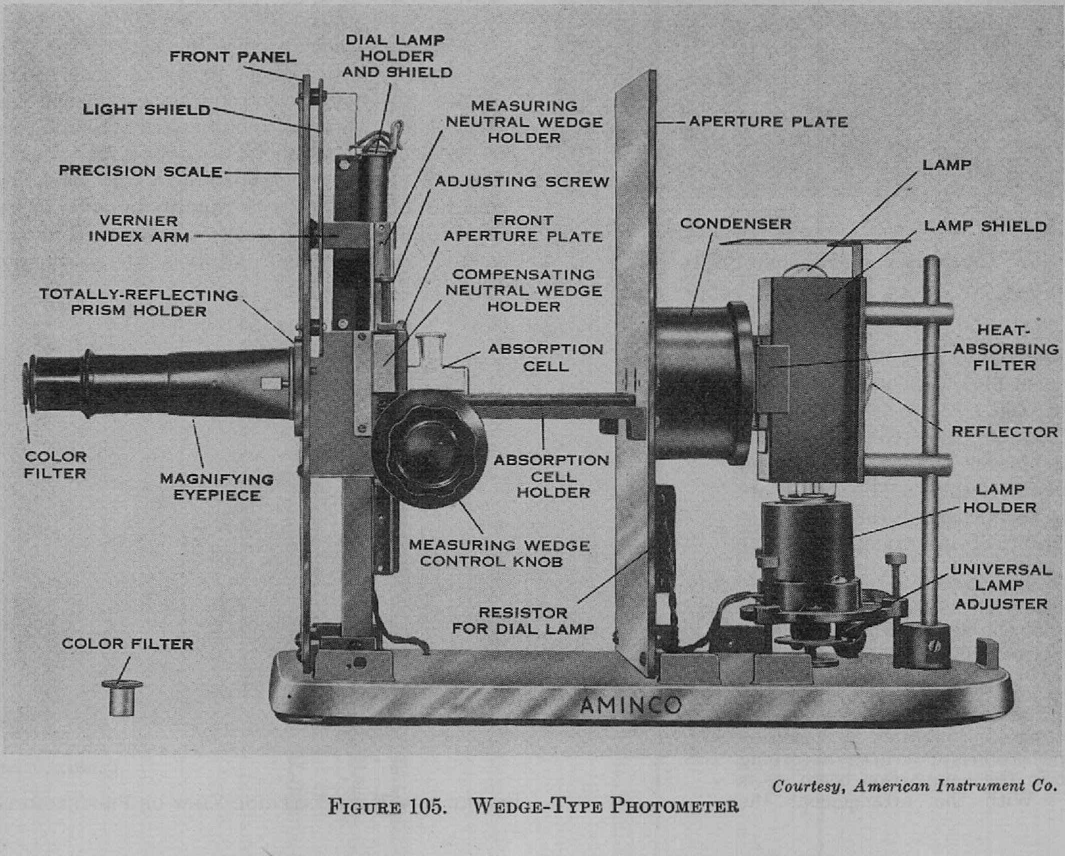
scribed (*196*, *222*). There still seems to be some objection to the inherent complication of phototube-amplifier combinations, but present trends in electronics already indicate a degree of reliability, extraordinary sensitivity, and good stability from this combination. Without going into the endless intricacies of this field, it may be mentioned that three relatively recent developments will exert an enormous effect on this class of photometers and probably stabilize practice for some time to come.

1. Electronic stabilization of light sources (*196*).
2. Inverse feedback amplifiers of extraordinary stability (*222*, *272*).
3. Multiplier-type phototubes such as the recent R. C. A. 931.

Twin-Cell Type. These may be of the barrier-layer or phototube class and in the latter case may or may not use amplification. Compensation can be attained optically or

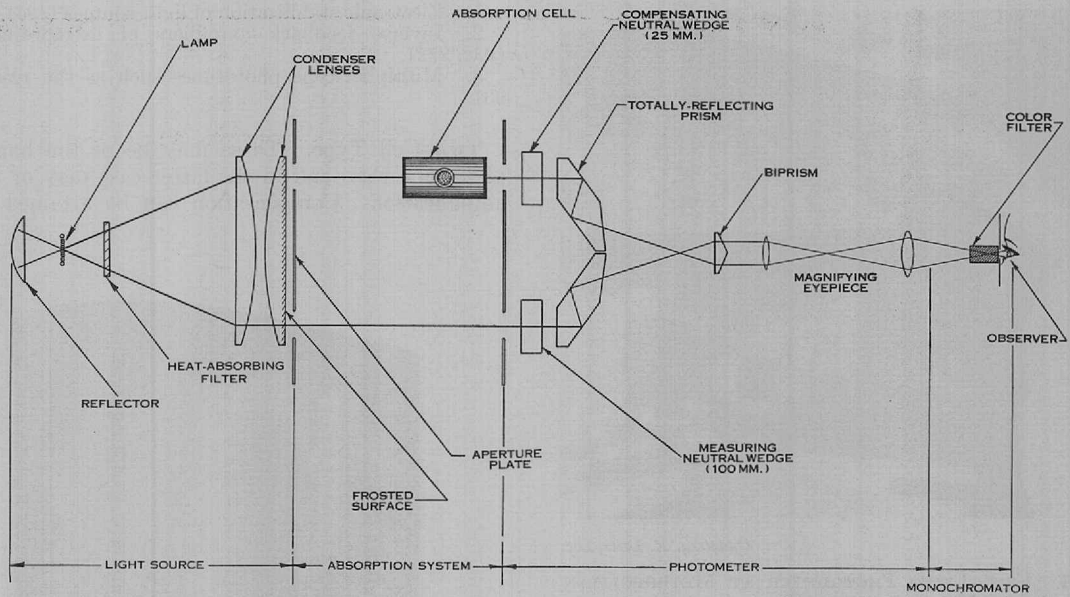
Courtesy, American Instrument Co.

Figure 104. Wedge-Type Photometer



Courtesy, American Instrument Co.

Figure 105. Wedge-Type Photometer



Courtesy, American Instrument Co.

FIGURE 106. WEDGE-TYPE PHOTOMETER

Courtesy, Central Scientific Co.

FIGURE 107. CENCO-SHEARD-SANFORD PHOTELOMETER

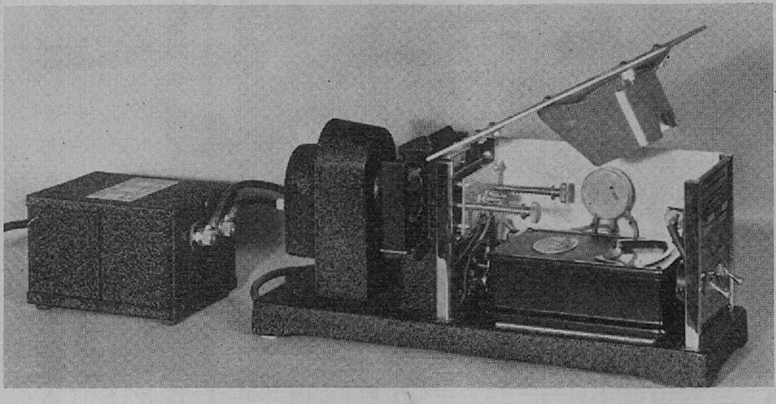
electrically and source fluctuations may or may not be cancelled, depending upon the method used (*196*). A higher differential sensitivity may be expected because the main output of each cell is canceled and only the differences due to absorption are measured or compensated for. Two examples of practical instruments will be mentioned.

The Spekker absorptiometer (Figure 110) employs a light source and two barrier-layer cells connected in opposition through a galvanometer. The absorption in the sample cell is compensated by opening a diaphragm until balance is restored. The drum controlling the diaphragm is calibrated in extinction units. Compensation is made in the absorbing side and not in the comparison beam, as is often done. With this arrangement the photocurrent in the measuring cell is restored to its original value, rather than decreasing the output of the comparison cell. This is a compact and carefully designed instrument worthy of the traditions of its manufacturer.

In Figure 111 is shown another twin-cell photometer using phototubes and a compensating electrical circuit. This circuit compensates for source variations and reads directly in per cent transmission, for which a decade resistor network is used. The circuit has been described by its inventors and representative results have been published (*252*), and the theory of balance has been discussed in relation to similar circuits (*196*).

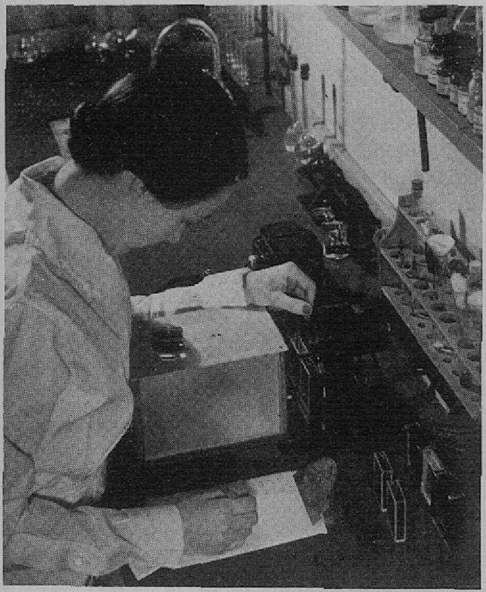
The photoelectric equivalent of the Aminco Wedge photometer which uses electrical compensation is shown in Figures 112, 113, and 114.

A comprehensive review of this subject is badly needed, particularly with respect to circuit analysis and the discussion of the newer electronic developments. In general, no very high degree of photometric precision is obtained in photoelectric photometers; the fact that most of the "colorimetric" chemical methods are so very sensitive and produce measurable "color" with minute amounts of substance often gives a false sense of precision and sensitivity to the measurement. On the other hand, it is interesting to compare these



Courtesy, Central Scientific Co.

FIGURE 108. SIDE INTERIOR VIEW OF PHOTELOMETER



Courtesy, Central Scientific Co.

FIGURE 109. USE OF PHOTELOMETER IN CLINICAL LABORATORY

methods with spectrographic techniques, where a precision of 2 to 3 per cent is generally considered excellent. In some cases the range of sensitivity for a given constituent is about the same, although in others the spectrograph is far more sensitive.

APPLICATIONS. A large number of applications of the visual types of photometers are classified with references and titles in the works of Urbach (*285A*), Krebs (*162*, *311*), and Heilmeyer (*114*), and in bulletins by Carl Zeiss, E. Leitz and Co., and the American Instrument Co. In addition, the treatises on colorimetry by Yoe (*309*) and Snell (*262*) contain specific reference to the use of photometers, both visual and photoelectric. All other analyses listed by them are suitable for use with any of these instruments, although if they were developed for use with a Duboscq colorimeter or comparison tubes, the necessary information relating to proper filters, etc., will be lacking (see also *99*).

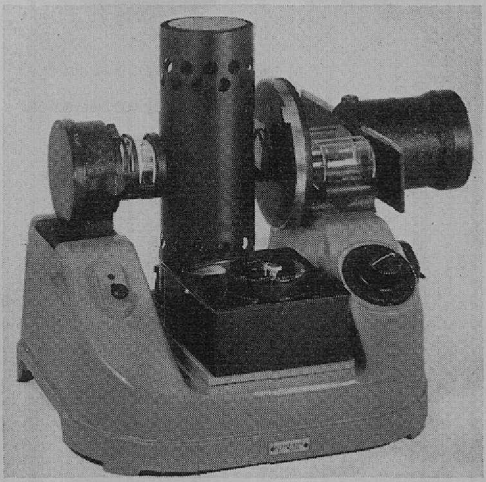
The principle of photometric titration has been employed from time to time in order to substitute titrimetric precision for a single photometric measurement, or better stated, to combine the photometric technique with that of titration. The arrangement shown in Figure 115 has been used in the author's laboratory for this purpose. The apparatus has somewhat wider utility, since it is automatically recording and therefore suited to follow slow changes in transmission.

It consists of an electronically regulated light source constant to 0.02 per cent, which illuminates the slit of a monochromator. A titration cell receives the monochromatic light which, after traversing the cell, strikes a vacuum phototube. The phototube and preamplifier are in a light-tight case to the right of the titration vessel. The photocurrent is fed to a high-gain inverse-feedback amplifier which delivers a linear 10-milliampere output for very low levels of illumination (exit slit of monochromator $\simeq$ 1 mμ = 10 Å.). The stability and linearity of this amplifier are high enough to require an output meter accurate to 0.1 per cent, which accounts for the precision standard meter visible in the foreground. For recording purposes, the output current may be sent through a standard series resistor box, the terminals of which are connected to a Micromax recording potentiometer.

Some typical photometric titrations to test Beer's law are shown in Figure 116. The readings as well as the records are transmission values and have been recalculated to extinction values, and corrections for dilution due to the addition of reagent have been made. This equipment is primarily for research on systems of analytical interest—i. e., to test Beer's law, study equilibria and rate of reaction, and establish stoichiometric ratios and thereby ascertain the nature of the light-absorbing entity.

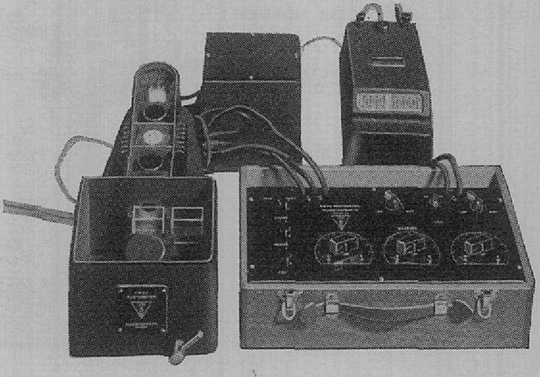
"Colorimetric"

This term, as understood by the chemist (*196*), refers to the analytical method whereby the concentration of a substance is determined by means of its color or by a color produced upon the addition of a suitable reagent. It is one of the most widely used analytical techniques and is primarily suited for very small amounts or concentrations. The methods of measurement vary from simple comparison in test tubes or Nessler tubes to the use of elaborate instruments. In the extension of the technique to more and more refined measurements it reduces to a photometric or a spectrophotometric problem. The compilation of colorimetric methods is tremendous and many treatises discuss the various instruments in detail (*80*, *262*, *309*). In many respects colorimetric methods compare very favorably with other analytical techniques such as the spectrograph, polarograph, etc., in sensitivity and precision.



Courtesy, Jarrell-Ash Co. and Adam Hilger, Ltd.

FIGURE 110. SPEKKER ABSORPTIOMETER



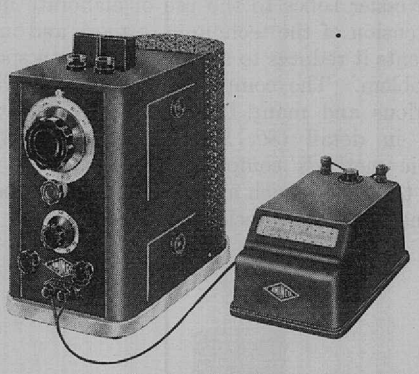
Courtesy, Wilkens-Anderson Co.

FIGURE 111. TWIN-CELL PHOTOMETER

Theory. Colorimetric matching involves the comparison of a colored sample, with or without instrumental aid, with a reference sample which may be an artificial reference or one which is identical in nature but of known concentration. In general, white light is used for the matching and some degree of hue discrimination as well as intensity matching is involved. If colored or filtered light is used, the technique is more properly called filter photometry. One principle of comparison involves the choice of suitable depths of solution (standard and unknown) until the two colors match, and under these conditions the respective concentrations are inversely proportional to the corresponding depths.

$$c_1t_1 = c_2t_2$$

This is a consequence of the Lambert-Beer law discussed above.



Courtesy, American Instrument Co.

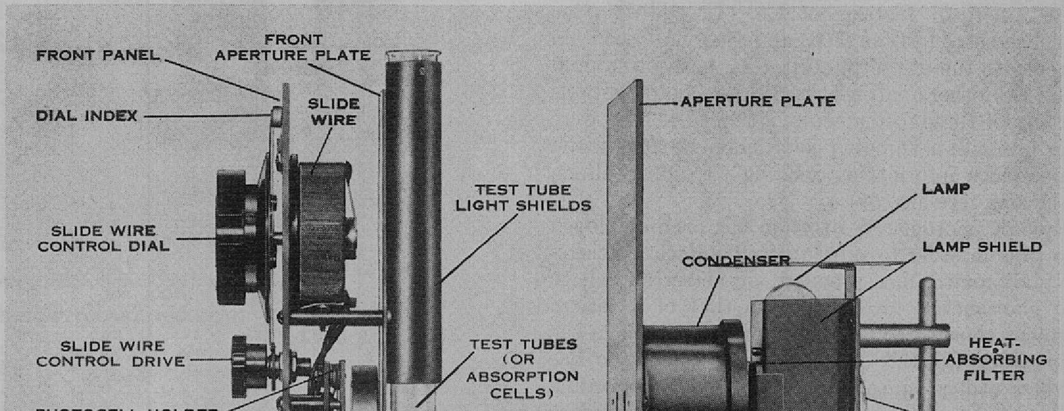
Figure 112. Photoelectric Photometer

Special cases arise in which the equilibrium between two colored species is to be determined, as, for example, in some pH measurements. These are discussed below.

Instruments. No discussion of test tube or Nessler tube comparison is called for here, since these are not instrumental methods, although numerous aids, such as comparator blocks or roulette comparators, are very useful accessories.

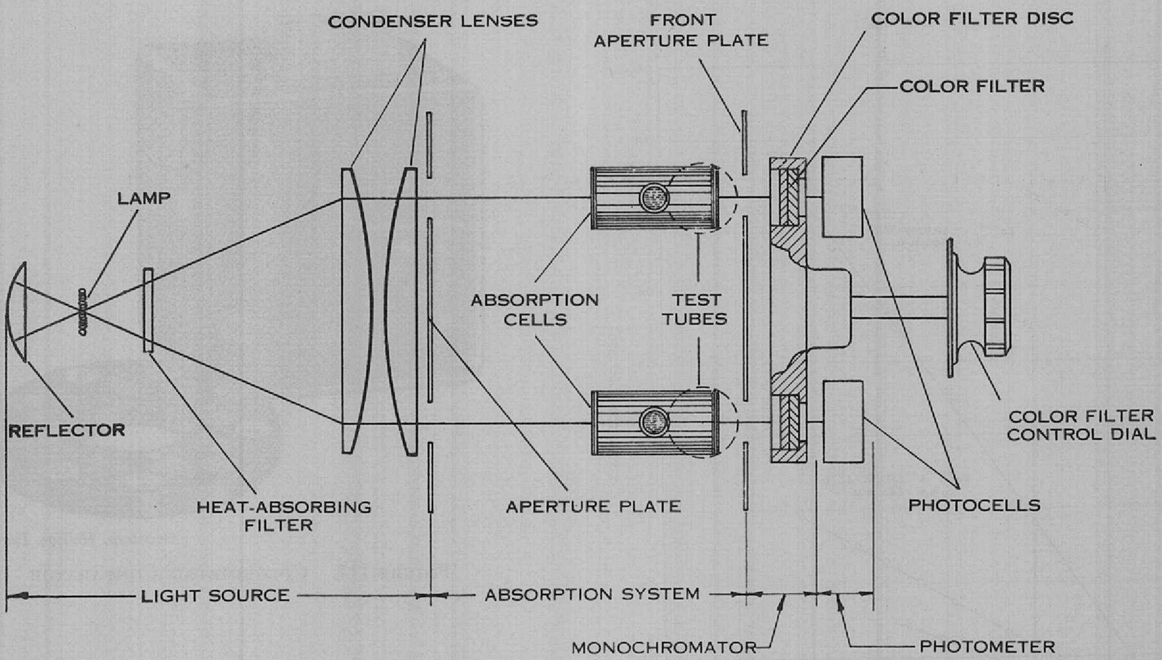
A very convenient comparator, shown in Figure 117, is one of numerous models manufactured by the company. The sample is placed in one of the fused-glass rectangular tubes and a similar tube is filled with distilled water. An appropriate color wheel or disk is then introduced, which upon rotation introduces nonfading glass color disks into the optical path. When one is found which matches the sample, its designating number is read at the aperture on the lower right. A simple eyepiece with prism brings the two color fields in juxtaposition. The comparison tube also serves to compensate for any turbidity or background color in the sample. Color disks are provided for twenty-four different pH indicators, for iron, ammonia, nitrite, chlorine, manganese, dissolved oxygen, lead, phosphate, silica, sulfides, and many other colorimetric methods. Color disks are also available for special classes of work, such as the color determination of petroleum oils and petrolatum, color of varnish, resins, lacquers, etc. Instruments of this sort are well suited for rapid, reasonably precise tests in routine or field work.

A familiar class of instrument is the Duboscq colorimeter, of which there are many models and types (*197*, Figure 60). Figures 118 and 119 illustrate two models that find extensive use in industry and in the clinical field. Modifications of the general principle adapt this class of instrument to special problems as, for example, the hemoglobinometer, the microcolorimeter, and the hydrogen-ion colorimeter. In the latter, unique provision is made for the measurement of equilibrium between the two colored forms of an indicator. The principle



Courtesy, American Instrument Co.

Figure 113. Photoelectric Photometer



Courtesy, American Instrument Co.

Figure 114. Photoelectric Photometer

is described in detail by Clark (*40*). In the expression relating pH to the apparent dissociation constant, K', of an indicator

$$\mathrm{pH} = \mathrm{p}K' + \log a/(1 - a)$$

the fraction, a, of the indicator which is in one of the colored forms and the other, $1 - a$, can be measured colorimetrically, and hence, knowing pK', the pH can be computed.

The hydrogen-ion colorimeter uses twin cups on either side. On the compensating side, one cup contains indicator in the acid form, the other cup in the basic form. The total depth is held constant, but by moving the inner cup, any hue ranging from the complete acid color to the full basic color can be obtained and the cup settings yield the ratio $a/(1 - a)$. Log tables of these ratios are provided, and the appropriate values are simply added to the correct pK' for that indicator.

Applications. There are so many applications of this method and in general they are so familiar that it is pointless to enumerate even typical examples (*6*). In clinical chemistry a very appreciable fraction of all analyses are conducted in this manner, because the method is rapid, requires very little material, and is sufficiently precise for the purpose. A tremendous amount of research and ingenuity has gone into the development of colorimetric chemical procedures; indeed, many substances by nature are not addicted to the formation of colored compounds and it has required clever indirect methods to bring them within the scope of this subject. Instruments for the purpose are relatively cheap, convenient, and versatile. The competition which photoelectric photometers have occasioned is real, but the simplicity and directness of the colorimeter will continue to be attractive for some time to come.

Courtesy, New York University

Figure 115. Manual and Recording Photometric Titration Apparatus

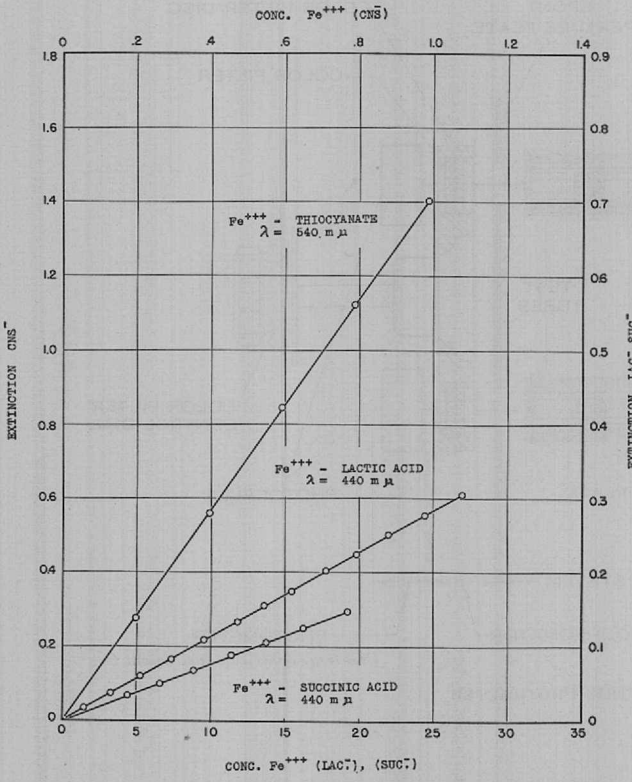
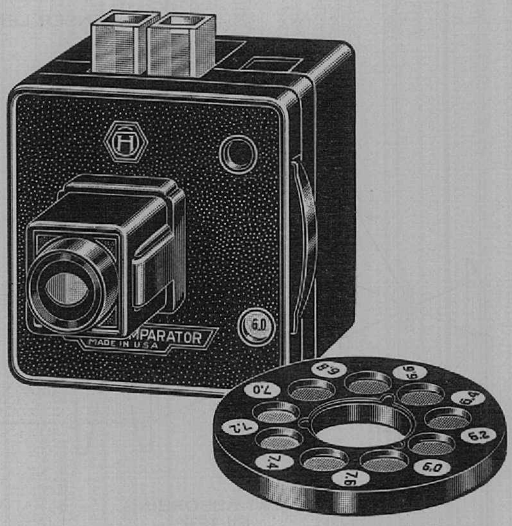
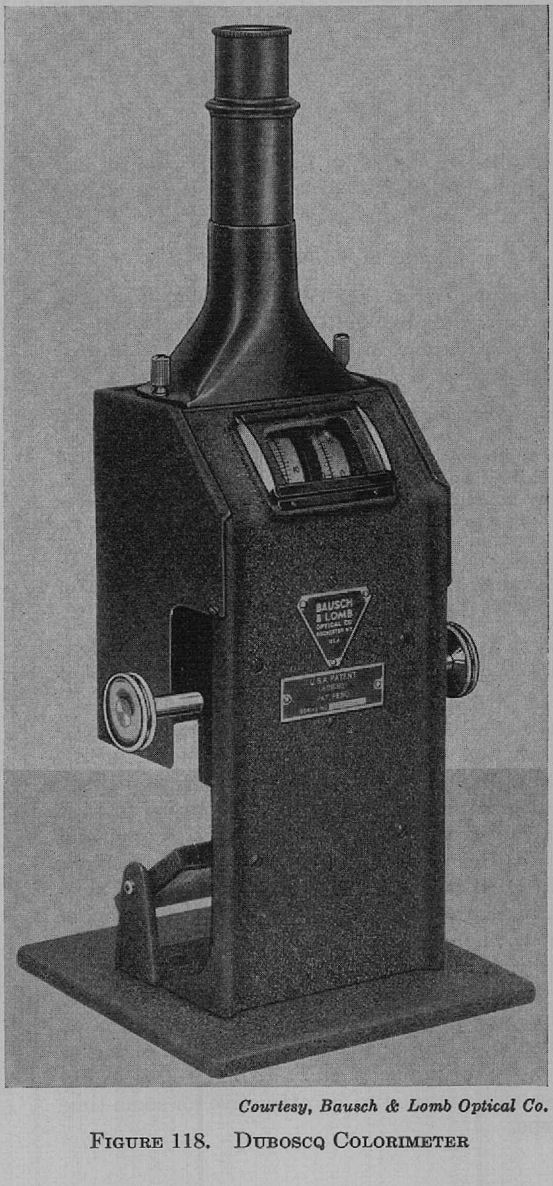


Figure 116. Photometric Titrations



Courtesy, Hellige, Inc.

Figure 117. Colorimetric Comparator



Courtesy, Bausch & Lomb Optical Co.

Figure 118. Duboscq Colorimeter

Fluorometric

Early studies in fluorescence were devoted to the elucidation of the phenomenon, the connection between chemical constitution and fluorescing ability, and a study of the factors which affect the phenomenon. It is an extremely complex phenomenon and although known, by a few examples, to the ancients it was often demonstrated but rarely used. Analytical uses were proposed a long time ago and several treatises (*48*, *220*) list hundreds of tests and analytical schemes. Although the phenomenon is common, it is more frequently associated with substances of limited analytical interest. Nevertheless, there are enough cases to make it worth while, and especially in the case of vitamin assay, important enough to stimulate the development of suitable instruments.

Theory. The fundamentals of the phenomenon are discussed at great length in two monographs (*79*, *219*). Upon absorption of light, a fluorescing substance re-emits the energy, generally at wave lengths longer than the exciting radiation (Stokes' law). In many systems and at extremely low temperatures definite energy states in the emitting system can be recognized, but at higher temperatures and especially in solution, the fluorescence spectrum is a broad "washed-out" band. The theoretical requirements of the quantum theory are obeyed in the energy distribution, as shown by Wawilow (*292*). The energy re-emitted is not directly proportional to the concentration—i. e., there are self-quenching effects. What is more important is the fact that many ions exert a powerful quenching effect on the fluorescence. The various effects which have an important bearing on analytical applications can be stated briefly. The specific fluorescence depends on (1) concentration of the fluorescing substance, (2) wave length of excitation, (3) pH, (4) temperature,

(5) presence of foreign ions, and (6) presence of other fluorescing substances.

The effect of pH is so pronounced that fluorescent substances have been used as "ultraviolet" indicators for titrations (*55*), although in view of (5) this is often attended by complications. The effect of foreign ions has been investigated in detail (*144*, *198*, *296*) and the information should be applicable to its influence on analytical uses of the method.

The general procedure consists in illuminating the sample with monochromatic ultraviolet light and measuring, either visually or photoelectrically, the visible fluorescent light which is emitted. As a whole, a true photometric method is to be preferred—that is, to measure the fluorescence per unit intensity of the exciting radiation. In some cases a choice of the exciting radiation with respect to wave length permits an analysis even in the presence of other substances which fluoresce.

INSTRUMENTS. The Pulfrich and Leifo photometers, previously mentioned, are available with suitable accessories for precise fluorescence measurements. Photoelectric fluorometers are becoming increasingly popular and already enjoy wide use, particularly in the vitamin field. The Hilger instrument shown in Figure 120 is an extension of the photometer absorptiometer, Figure 110. An external, sensitive galvanometer is used to indicate balance, which is achieved by optical compensation. One well-known instrument has been described (*197*, Figure 70) and one of its applications is illustrated in Figure 121. Another, using a phototube and stable amplifier, is shown in Figures 122 and 123. Excitation is provided by a mercury arc and suitable filters. Very simple controls adjust zero setting, a standard deflection in terms of a reference sample and a control for balancing out small initial deflections corresponding to the blank. Sensitivities several times as high as those obtainable with the simpler cell-galvanometric arrangement are claimed; on the basis of current practice in electronics this is a reasonable claim.

APPLICATIONS. These include the determination of vitamin B_1 (thiamin, *117*), B_2 (riboflavin, *117*), and all naturally fluorescing substances such as quinine, other alkaloids, oils, waxes, and proteins. Methods whereby nonfluorescing substances can be chemically treated to produce a fluorescing substance are discussed in reference works (*48*, *220*) and by White (*298*). Mention should also be made of the semianalytical applications in forensic work for the detection of adulterants, forgeries, and spots or suspected artifacts. These are usually accomplished by visual inspection or photography.

Turbidimetric and Nephelometric

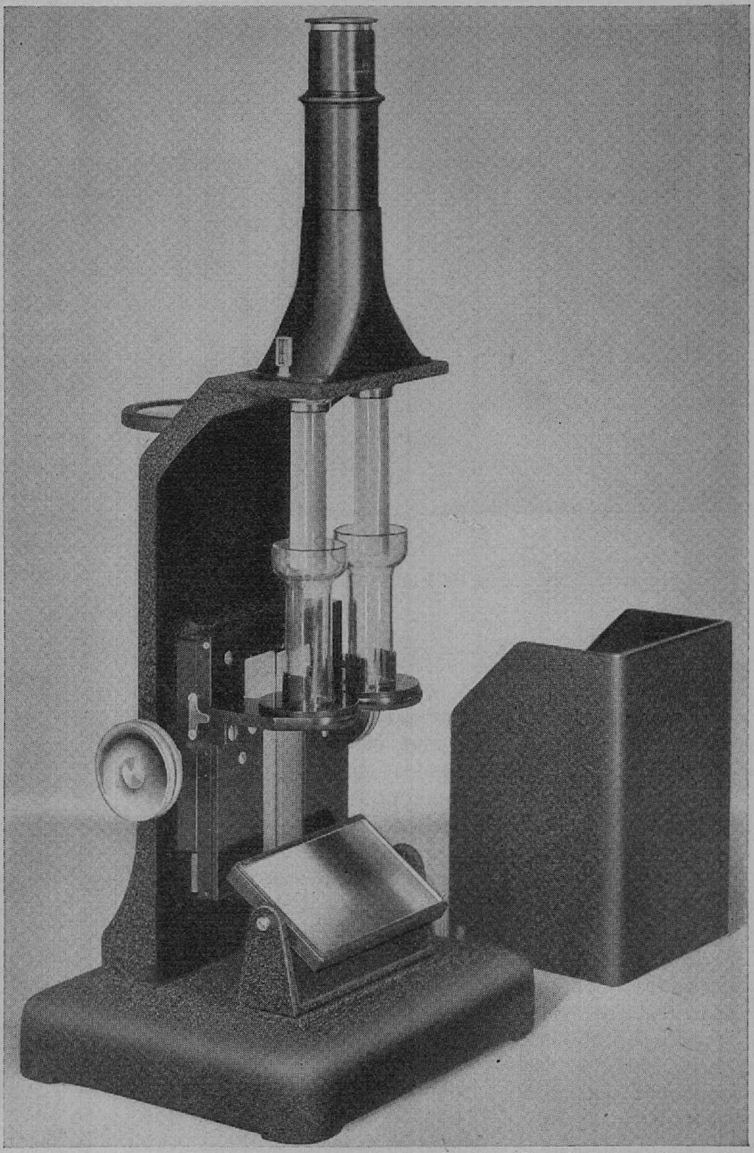
The optical properties of finely divided particles or disperse systems have some interest for the analytical chemist but considerably more interest for the colloid chemist who is interested in learning more about the nature of these dispersions. Since such dispersed systems scatter light, a suitable measurement of the light scattering may be used to determine the amount of dispersed material. Three methods may be used:

1. Light which has traversed a turbid medium will be scattered to some extent and there will therefore be a decrease in the intensity of the emergent beam.
2. The intensity of the light which is scattered laterally may be compared with a suitable reference and the procedure is then known as nephelometric.
3. An accurate measurement is made of the ratio of intensity of the scattered to the incident light by means of a Tyndallometer. The principle and design of this instrument were described by Mecklenburg and Valentiner (*189*); it is manufactured by Schmidt and Haensch of Berlin.

Light scattering is an extremely complex phenomenon and the theory of the phenomenon was given in detail by Lord Rayleigh (*294*), according to which the intensity of the scattered light is given by:

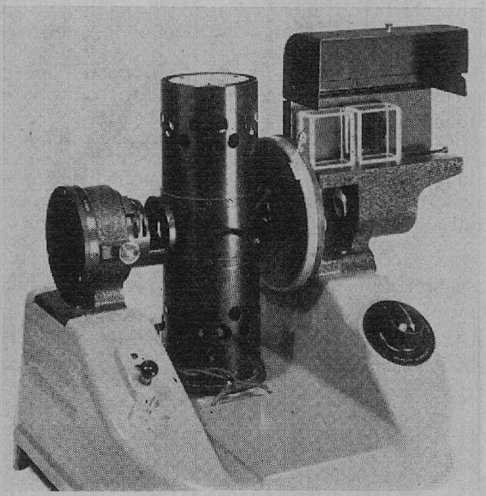
$$\frac{I}{I_0} = K \frac{Nv^2}{\lambda^4} \sin^2 \alpha$$

where I is the intensity of the scattered light viewed at an angle α to the primary beam of intensity I_0; N is the number of particles of volume v, and λ is the wave length.



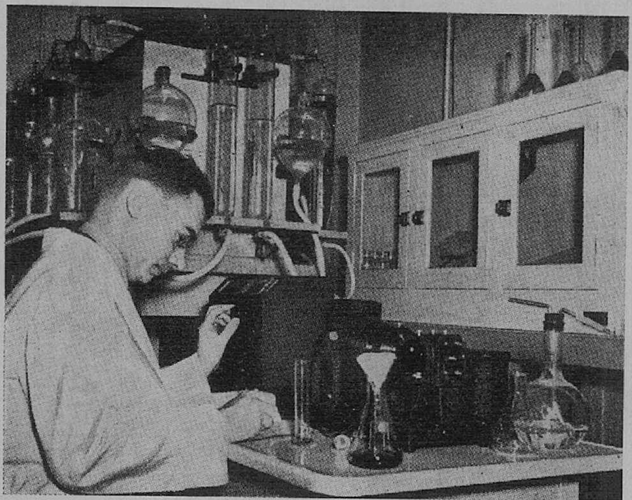
Courtesy, Bausch & Lomb Optical Co.

FIGURE 119. DUBOSCQ COLORIMETER



Courtesy, Jarrell-Ash Co. and Adam Hilger, Ltd.

FIGURE 120. SPEKKER FLUOROMETER



Courtesy, Pfaltz & Bauer, Inc.

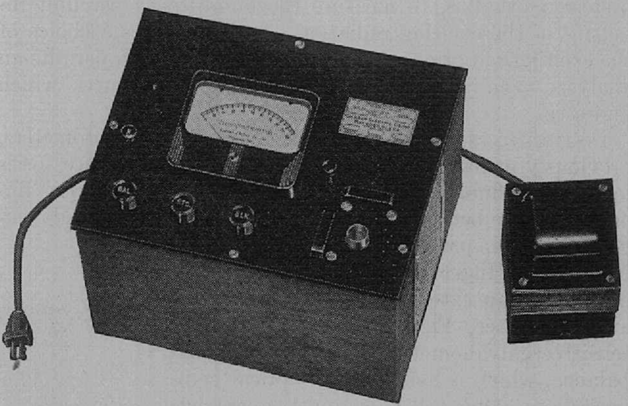
FIGURE 121. USE OF FLUOROPHOTOMETER

Of principal analytical interest is the fact that the measurements will be affected by (1) manner of mixing sample and reagent, (2) ratio of the concentrations, (3) rate of mixing, (4) rate of development to maximum turbidity, (5) temperature, (6) stability of the dispersion, and (7) effect of foreign substances—electrolytes and nonelectrolytes.

It is also assumed that the dispersed phase is colorless, for if colored dispersions are produced there is the added complication of selective light absorption.

A discussion of these complexities and a theoretical and practical treatment are available (*104, 153, 295, 309*, Vol. II).

INSTRUMENTS. Suitable instruments for the comparison of relative turbidities range from test-tube comparator blocks to more elaborate means of photometric comparison. An example of a very useful turbidimeter for sulfate determinations is shown in Figure 124. The estimation of turbidity with this instrument is obtained by measuring the depth of the suitably prepared dispersion through which one can still observe the filament of a small lamp. A plot of the thickness of liquid against the concentration of the dispersed phase yields a smooth curve, as shown in Figure 125. The photoelectric equivalent of this instrument is shown in Figure 126; the advantage of the second form lies in the more objective nature of the setting. Corresponding calibration curves for this instrument are shown in Figure 127. Both instruments have found wide application for this class of analyses, particularly in sulfate determinations, with which they are conveniently used in connection with the Parr sulfur bomb (Figures 128 and 129).



Courtesy, Coleman Electric Co.

FIGURE 122. PHOTOFLUOROMETER

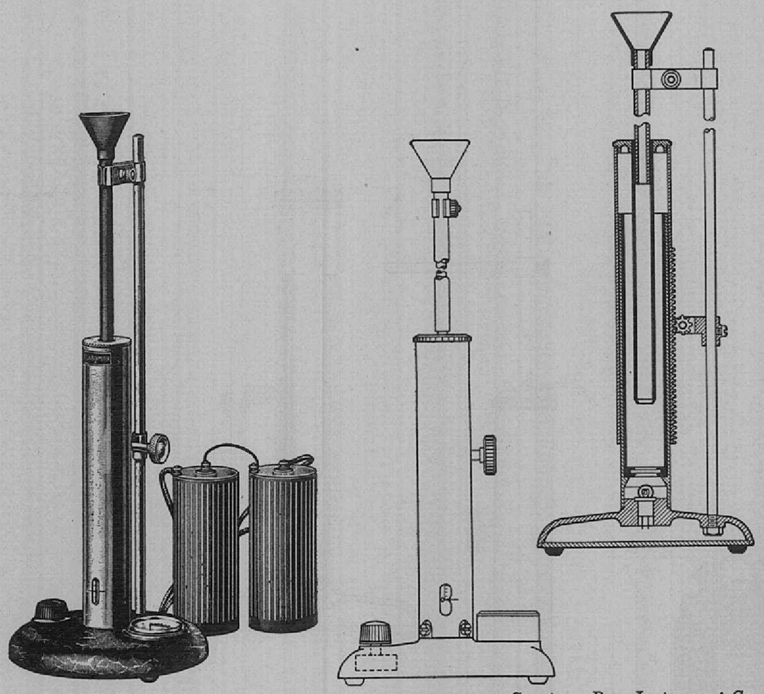
Another approach to the same problem is illustrated in the Hellige instrument (Figures 130 and 131), in which a twin photometric field results from the lateral illumination of the suspension and a comparison beam which is reflected upward through the system. The comparison beam may be adjusted by means of a precision slit (*S*, Figure 132).

Many of the commercially available photoelectric photometers are adaptable to turbidimetric measurements. In practically all cases such use implies empirical calibration, primarily to suit the optics of the system but more especially because of the great influence of the various factors noted above.

Several sources describe alternative optical approaches,

Courtesy, Coleman Electric Co. and Continental Can Co.

FIGURE 123. ELECTRONIC PHOTOFLUOROMETER IN CHEMICAL RESEARCH



Courtesy, Parr Instrument Co.

FIGURE 124. TURBIDIMETER

some of them based on the fact that the light scattered by such media is almost completely polarized.

APPLICATIONS. The method is particularly suited for the determination of small quantities of any substance which can be "precipitated" under conditions that will maintain a stable and uniform dispersion. An extensive list of such applications, along with detailed directions, is to be found in Yoe's monograph (*309*, Vol. II) and some later applications, particularly by photoelectric means, have been mentioned by the author (*196;* see also *27*, *102*, *267*). An interesting extension of the technique has been described by Goodhue (*98*), who developed a turbidimetric titration scheme for the determination of small amounts of nicotine (see also *15*). There have also been many applications of these methods to problems of no particular analytical interest, such as the determination of sedimentation rates.

What has been said about these measurements applies also to dispersions in gases and has proved very useful in the examination of very dilute smokes and vapors.

Refractometric

The refractive index of a medium is an important constant and has useful analytical applications. It can be measured in any region of the spectrum from electric waves to the shortest x-rays, and in all states of aggregation, solid, liquid, or gas. Although it is an unspecific property, in many instances its numerical value is an important identifying characteristic which, in connection with other properties, defines the system. It finds many uses in technical analysis for control of purity and the analysis of simple binary mixtures.

THEORY. The refractive index, n, expresses the ratio of the velocity of light in the two media which form the boundary. The law of Snell expresses n as the sine of the angle of incidence divided by the sine of the angle of refraction or

$$n = \frac{\sin i}{\sin r} \qquad (4)$$

The specific refraction may be expressed according to Gladstone and Dale as

$$R = (n - 1)/d \qquad (5)$$

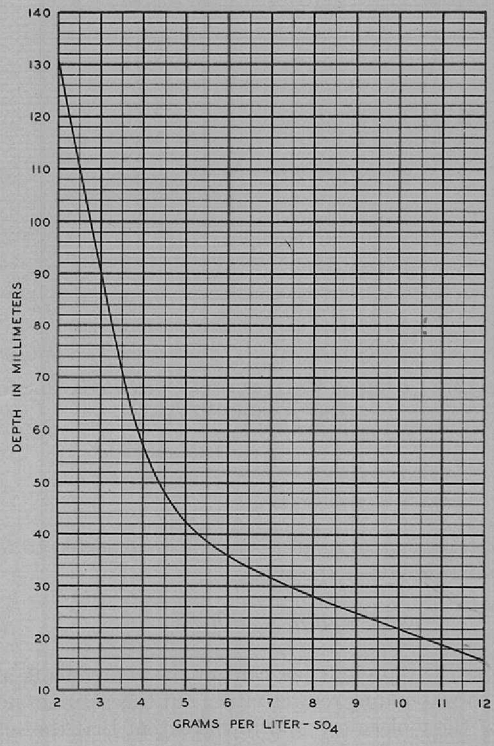
where d is the density, or somewhat better by the Lorenz-Lorentz equation

$$R = \frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d} \qquad (6)$$

The product of this quantity and the atomic or molecular weight yields the atomic refraction or molecular refraction. The sum of the atomic refractions is equal to the molecular refraction, provided the necessary corrections are made for the binding or linkages. The contribution of double and triple bonds and conjugated linkages has been evaluated, and in the early applications these data are very useful in establishing the structure of complex organic compounds. Small constitutive variations in these corrections are now recognized and the problem is not so simple as the early considerations indicated.

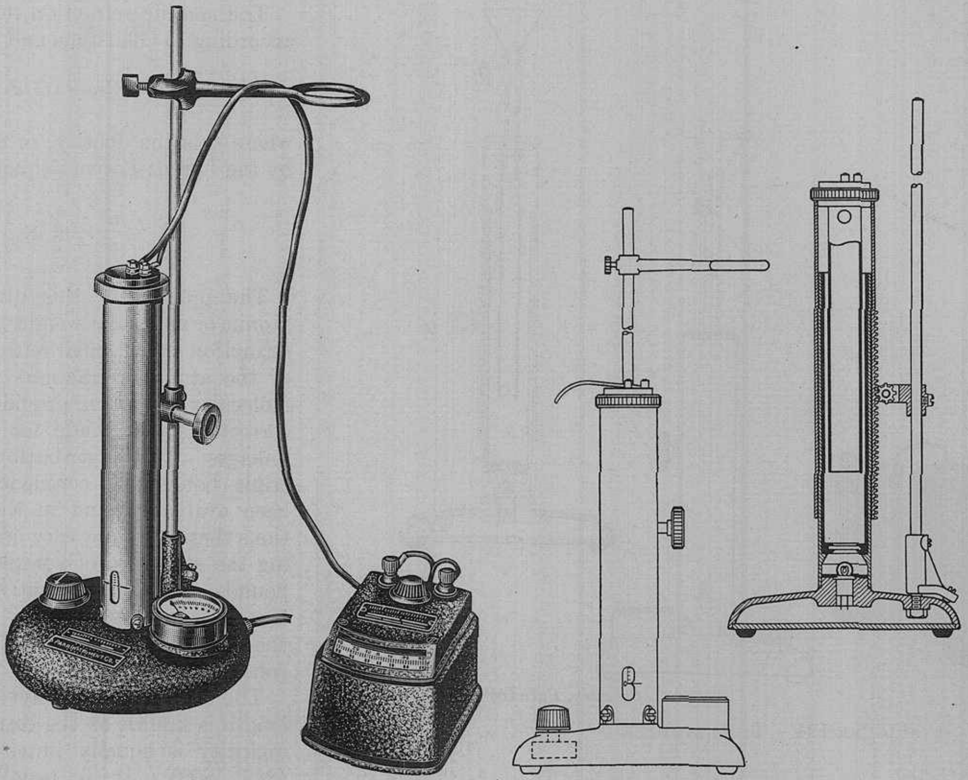
The change in refractive index with wave length is known as the dispersion, and this quantity is equally important and useful (*289*, *302*). It is usually expressed as $(n_F - n_C)$ where the subscripts refer to the hydrogen lines, F = 4861 Å. and C = 6563 Å.

The connection between Equation 6 and the total polarization, P, as determined from the dielectric constant is discussed under the latter heading.



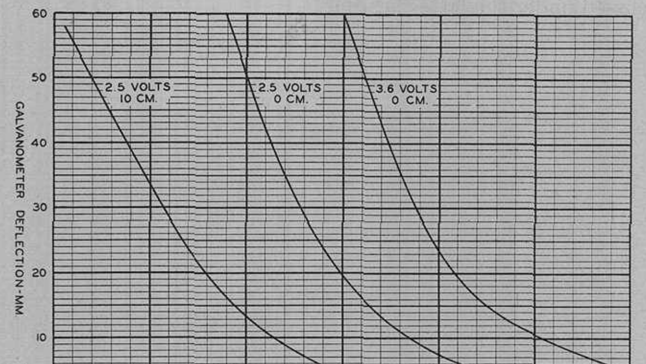
Courtesy, Parr Instrument Co.

FIGURE 125. TYPICAL CALIBRATION CURVE FOR VISUAL TURBIDIMETER



Courtesy, Parr Instrument Co.

Figure 126. Turbidimeter, Photoelectric Type



Courtesy, Parr Instrument Co.

Figure 127. Typical Calibration Curve for Photoelectric Turbidimeter

The refractivity of mixtures might be expected to follow a simple mixture law of the type

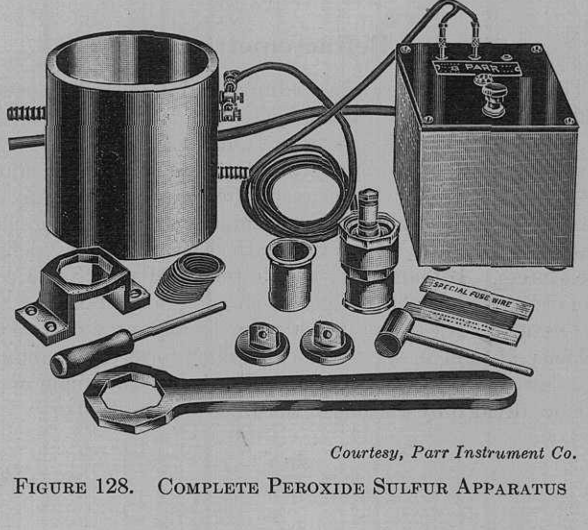
$$100\,R = P_1R_1 + P_2R_2 + \ldots\ldots$$

where the P's represent per cent of the components and the R's the corresponding refractivities, but this assumes no interaction of the molecules; and to the extent that the solutions deviate from ideality one can expect this to appear in the total refraction. In most cases a mixture is analyzed by reference to the refraction of mixtures of known composition.

Both refractive index and dispersion vary with the temperature; in solutions the temperature coefficient is usually large and negative in sign.

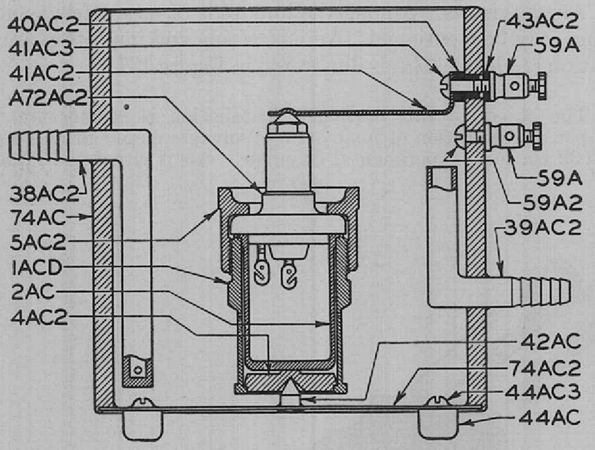
Instruments. Many simple devices may be used for a rough measurement of n (*152*), and the ordinary microscope may be used for this purpose if no refractometer is available. These methods are discussed in standard works on optics (*294*). Four general classes of instrument will be mentioned.

Abbe Refractometer. This instrument is direct-reading in refractive index for the sodium lines, n_D, with a range of about 1.3 to 1.7 and can be estimated to ±0.0001. Solids or liquids within this range can be measured. For liquids only a drop is necessary



Courtesy, Parr Instrument Co.

Figure 128. Complete Peroxide Sulfur Apparatus



Courtesy, Parr Instrument Co.

FIGURE 129. SULFUR BOMB AND WATER BATH

and it is held between two prisms. The prism mountings are hollow, permitting the use of circulating water from a thermostat to maintain constant temperature. The principle depends upon the critical angle of total reflection which is determined by n of the liquid and the constant, n, of the contiguous prism. White light may be used as the source and an Amici prism is used to cancel dispersion effects. When the prism is rotated to produce an achromatized shadow edge, the sodium line passes through undeviated. The angular setting of the Amici compensator enables one to obtain the dispersion. Tables are usually supplied for this information. Several examples of this instrument (*196*, Figure 53) are illustrated in Figure 133. Special scales can be provided for an Abbe refractometer for use as a direct butyrorefractometer, sugar refractometer, etc.

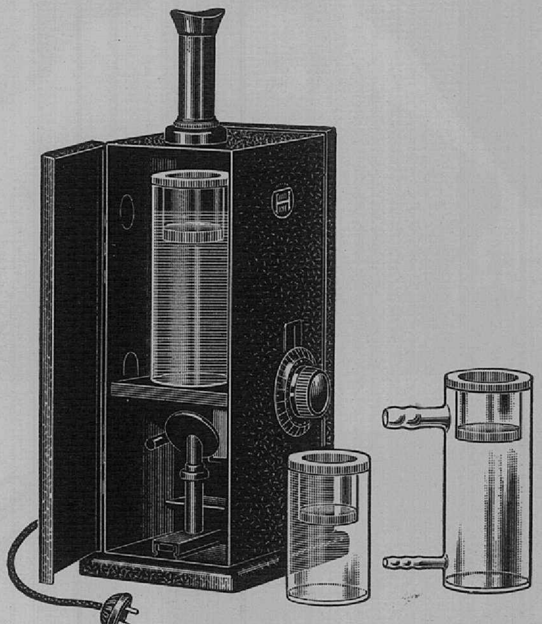
Pulfrich Refractometer. This instrument also employs the total-reflection principle and is particularly suited for the determination of dispersion values. It is not direct-reading; the angle of the deviated ray is referred to tables from which n may be obtained. No achromatizing arrangement is provided, so that full dispersion is observed in the eyepiece. In its ordinary form n can be determined to ±0.0001, but more elaborate forms of the instrument have reduced the uncertainty to ±0.00001. This instrument is manufactured by Carl Zeiss and by Adam Hilger. A full description is given in most texts on optics and physical chemistry.

Dipping Refractometer. This is a limited-range instrument with correspondingly higher precision. In order to cover the entire range, interchangeable prisms are provided and as many as a half dozen may be required. A typical instrument is shown in Figure 134 and schematically in Figure 135. An arbitrary scale is mounted in the eyepiece and a rotating drum makes it possible to read the position of the dividing line on the scale to tenths of a division. The average precision is of the order of ±0.000035. A compensating prism is also used to achromatize the shadow edge. It is rotated by the knurled ring near the prism. The prism is usually dipped into a sample cup, but where limited amounts are available, a special cup may be used containing an auxiliary prism which nearly engages the hypotenuse face of the instrument-prism. A thin film of the liquid is thus caught between the two.

Interferometer. In a refractometer, the refractive index itself is measured, whereas with the interferometer the difference in refraction of two liquids or two gases is determined (*109, 294*). This is the usual case, although it is possible to calibrate an interferometer in absolute terms, using monochromatic light of known wave length. Since a change in refractive index results in a change in the velocity of light through the medium, it will be apparent from the definition of n that to measure n we need but measure the difference in velocity. Light coming from a common source and traveling in two separate beams along the same distance will arrive in phase at any point, but if one path is through a medium of slightly higher refractive index, this is equivalent to a virtual change in distance traversed and the two beams will be out of phase and show interference fringes. The phase difference can be restored by moving a compensator plate driven by a slow-motion screw.

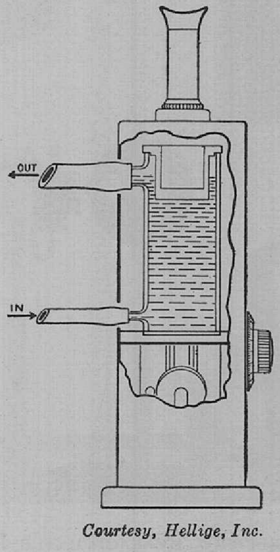
Any interferometer can be used to demonstrate this principle, but for exceedingly small differences it is necessary to bring the two arms together in order to rule out any appreciable temperature differences. Under the best conditions, values a thousand times smaller than those measurable with a refractometer can be determined.

For example, in the case of gases with a 100-cm. chamber, the error is of the order of $2 \times 10^{-8}\ n$. For liquids in 8-cm. depth about $\pm 2.5 \times 10^{-7}$ and at 1-mm. depth about $\pm 2 \times 10^{-5}$. With the gas interferometer shown in Figure 136, a



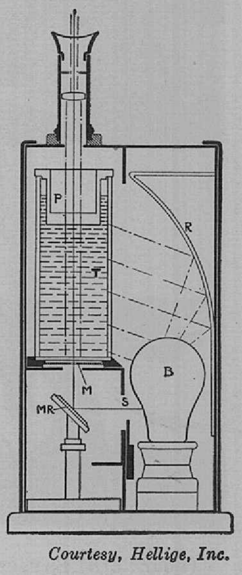
Courtesy, Hellige, Inc.

FIGURE 130. HELLIGE TURBIDIMETER



Courtesy, Hellige, Inc.

FIGURE 131. HELLIGE TURBIDIMETER FOR CONTINUOUS READING



Courtesy, Hellige, Inc.

FIGURE 132. HELLIGE TURBIDIMETER, DIAGRAMMATIC VIEW

portable instrument with a 10-cm. chamber, the error in measuring carbon dioxide, methane, or hydrogen in air amounts to about 0.1 per cent. The same instrument can be fitted with 25- and 50-cm. chambers; the errors are then 0.04 and 0.02 per cent. It is suited for rapid "on the spot" analyses of noxious fumes, carbon dioxide in expired air, or ether in the atmosphere of operating rooms (±0.4 to 0.8 gram per cubic meter).

APPLICATIONS. Among the hundreds of uses a few typical ones may be mentioned. An interesting and important application (*149, 243, 249*) is illustrated in Figure 137.

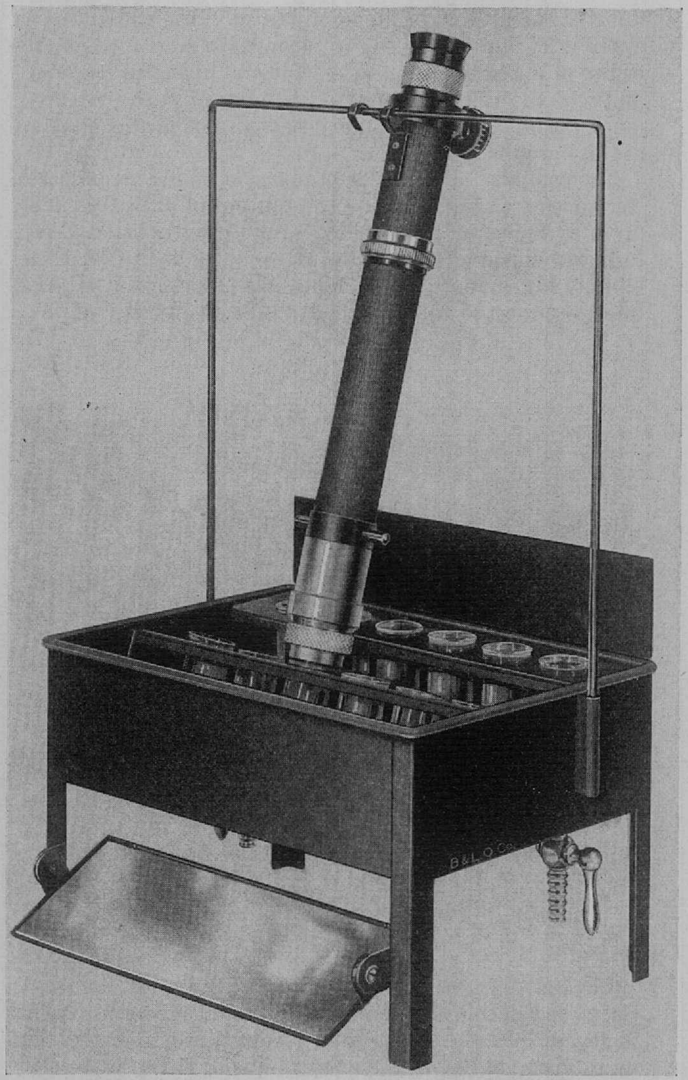
The object of this particular installation is to measure the vapor concentration of toxic organic solvents in the air of a large (1032 cu. feet) experimental chamber. Air is circulated rapidly

FIGURE 133. (*Upper Left*) JELLY-TYPE REFRACTOMETER FOR USE WITH A DROP OF LIQUID
Courtesy, Fisher Scientific Co.

(*Left Center*) ABBE TYPE REFRACTOMETER
Courtesy, Spencer Lens Co.

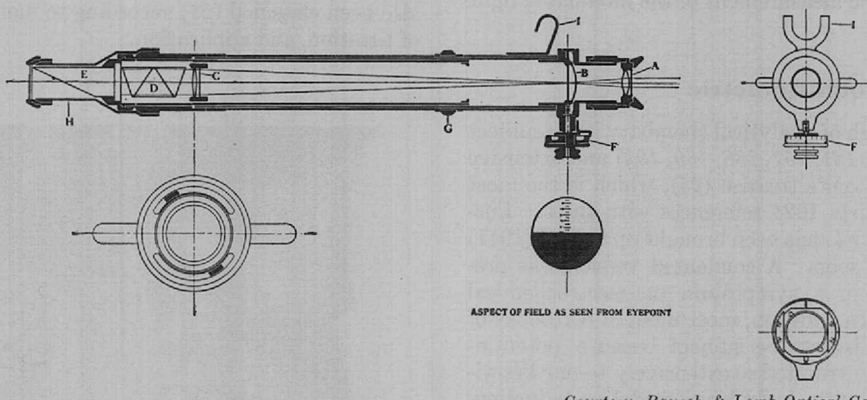
(*Lower Left*) BAUSCH & LOMB PRECISION REFRACTOMETER–PULFRICH PHOTOMETER AS USED FOR MEASUREMENTS ON SUGAR SOLUTIONS. *Courtesy, F. W. Zerban, New York Sugar Trade Laboratory*

(*Upper Right and Right Center*) VALENTINE REFRACTOMETER, IMPROVED ABBE TYPE
Courtesy, Industro-Scientific Co. and Gamma Instrument Co.



Courtesy, Bausch & Lomb Optical Co.

Figure 134. Dipping Refractometer



Courtesy, Bausch & Lomb Optical Co.

Figure 135. Sectional Views of Dipping Refractometer

by means of a fan in a set of recirculation ducts. One hundred and thirty cubic feet per minute of fresh air are supplied, which is sufficient to eliminate the building up of carbon dioxide and water vapor in the chamber and to prevent the upset of the basic oxygen-nitrogen relation even when three subjects are in the chamber. Fresh drying tubes containing calcium chloride to remove water vapor and Ascarite to remove carbon dioxide are converted between the sampling ducts and the interferometer chamber. The instrument must be shielded from air currents (avoiding thermal gradients) during measurements. Concentration of toluene vapor ranging from 25 to 1000 parts per million in air can be measured and the instrument has also been used for determining the concentrations of vinyl cyanide vapors.

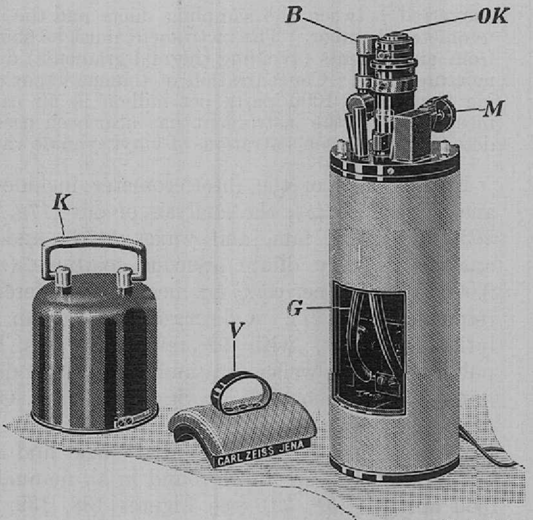
Further uses of the interferometer include gas analysis (*218, 248*), the analysis of oils (*172, 186, 203, 237, 290*), fats, and waxes (*173*), and the analysis of very dilute aqueous solutions (n = 0.0004 to ±0.1 per cent) by means of a differential refractometer (*221*). A discussion of n as an analytical constant, with 92 references, has been published by Fulweiler (*83*) and a means for determining fat in chocolate by Stanley (*266*). Other uses have been practiced for such a long time that they are almost taken for granted; sugar and alcohol tables (*253*) are to be found in all manuals of food analysis (*31, 32*) (see Figures 138, 139, and 140), and many other systems of analytical utility (*164, 182*) are listed in International Critical Tables and related compilations (*175, 229*).

Polarimetry

The rotation of the plane of polarized light has long been a convenient means of analysis, limited, of course, to systems containing molecules with an asymmetric atom, the most common of which is carbon, but amenable to many compounds of sulfur, tin, selenium, silicon, and pentavalent nitrogen. The technique is confined mostly to the analysis of sugars (*31, 32, 140*), essential oils, and alkaloids.

Instruments and Methods. Representative examples of this instrument are shown in Figure 141. The polarimeter shown in Figure 142 contains all the refinements for very precise work, including preliminary purification of the light by a monochromator. A splendid example of a precision installation is shown in Figure 143. The polarimeter shown in Figures 144 and 145 is an interesting example of the utilization of that versatile product of modern times—polaroid film. This presents for the first time a very economical means of demonstrating the principle of the polarimeter, yet providing results sufficiently accurate for a considerable number of useful and practical analyses.

Applications. Extensive tables are available in the literature (*31, 32, 139, 168, 225, 283*) for the specific rotation



Courtesy, Carl Zeiss

FIGURE 136. GAS INTERFEROMETER

of a large number of substances, as well as tables in a more convenient form for definite analytical applications. In many instances a combination of the specific rotation plus the rotatory dispersion is useful for identification or for special analyses.

While optical rotation is restricted in its applicability, magneto-optic rotation applies to all substances and in all states of aggregation. This Faraday effect, the numerical value of which is expressed as the Verdet constant, is known for thousands of substances. It has found no practical use in analytical chemistry, largely because of experimental and manipulative complications. Then, too, because of its perfectly general and unspecific nature it is not likely to be of greater use in the future unless experimental simplifications are forthcoming. The magneto-optic effect can be multiplied by repeated passage of the light through the sample, which is not true of ordinary optical rotation.

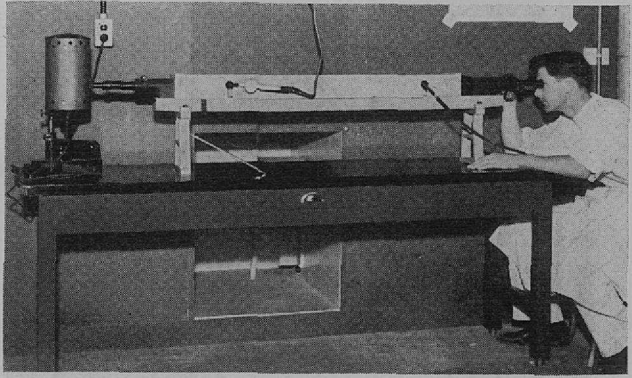
Some interesting possibilities seem to exist in the use of this principle combined with the use of an alternating magnetic field with a photoelectric measurement of the modulated light component (*201*).

Potentiometric

This important branch of analytical chemistry is the subject of several monographs (*131, 157, 158, 159, 194*) and extensive reviews (*25, 84*). Böttger's treatise (*25*), which is the most recent and complete, lists 1024 references with titles. Furman's excellent review (*84*) has been brought up to date (1941) and will be published soon. A condensed version was presented recently (*85*) in a symposium on electrochemical methods of analysis. In addition, most modern textbooks of analytical chemistry discuss the subject because potentiometric methods have contributed so extensively to our knowledge of equilibria, solubility, hydrolysis, oxidation-reduction, and the behavior of indicators. For our purpose it will suffice to outline the most important principles and indicate the advantages of this method of analysis.

THEORY. The potential at the electrode-solution interface may be used to obtain information which is analytically useful. For a limited number of electrodes and under suitable conditions, a single measurement of the potential with respect to a known reference electrode gives information which can be used directly. Thus the pH of a solution can be obtained from the hydrogen, quinhydrone, glass, and antimony electrodes. For the most part, changes in e. m. f. during the course of a titration impose less demand upon the reproducibility of the electrode and the number of such systems is much greater. Concentration cells and modifications thereof are also useful.

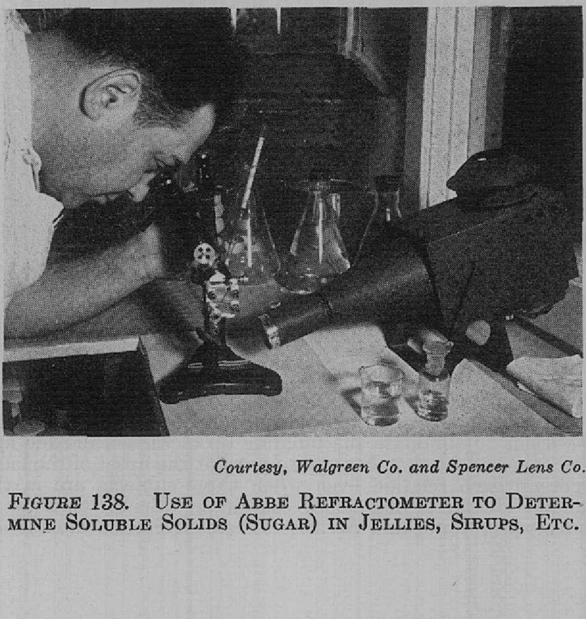
ELECTRODES. For the determination of pH a number of electrodes are satisfactory. The concept of pH as originally given by Sørensen, $pH = -\log c_{H^+}$, is often written to conform with modern concepts as, $pH = -\log a_{H^+}$. This is not entirely satisfactory, but it is possible to bring the pH scale into closer accord with thermodynamic quantities (*184*).



Courtesy, D. W. Armstrong and P. A. Cole, Division of Industrial Hygiene, U. S. Public Health Service

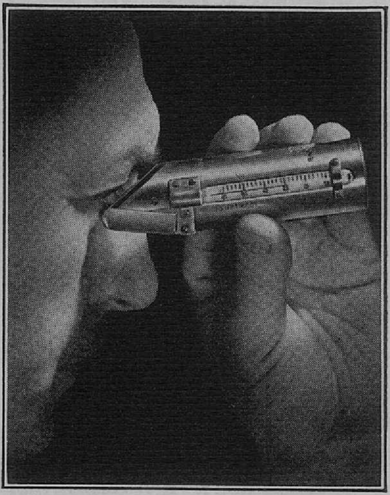
FIGURE 137. USE OF RAYLEIGH-JEANS INTERFERENCE REFRACTOMETER IN CONTROLLING CONCENTRATIONS OF ORGANIC VAPORS IN AIR

Electrode Systems and Methods. A very great number of electrode systems have been used; these have been classified in several places (*25, 84, 158*). Among them are the platinum, glass, antimony, hydrogen, quinhydrone, and silver-silver chloride electrodes, and many bimetallic systems. Exhaustive compilations of individual methods include acid-base (also in nonaqueous media), precipitation, oxidation-reduction, and concentration-cell techniques. These have also been classified (*25*) according to method, substance, class of titration, and application.



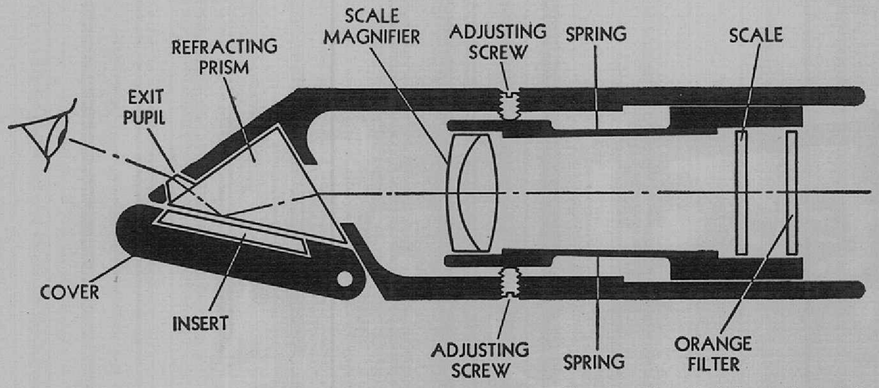
Courtesy, Walgreen Co. and Spencer Lens Co.

FIGURE 138. USE OF ABBE REFRACTOMETER TO DETERMINE SOLUBLE SOLIDS (SUGAR) IN JELLIES, SIRUPS, ETC.



Courtesy, Bausch & Lomb Optical Co.

FIGURE 139. HAND REFRACTOMETER



Courtesy, Bausch & Lomb Optical Co.

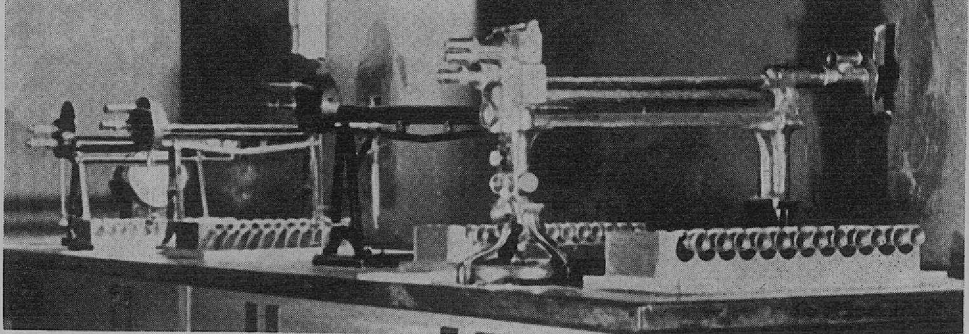
FIGURE 140. DIAGRAM OF HAND REFRACTOMETER

POTENTIOMETRIC TITRATIONS. A typical titration curve is shown in Figure 146, *a*, and in differential form at *b*. Curve *b* is obtained by plotting the change in potential per increment of reagent ($\Delta E/\Delta cc$) against the volume of reagent. Although a titration curve can be computed from the e_0 values, and the value of E at the end point can be predicted, this assumes a high degree of reproducibility of the electrode system and a more or less definite and constant ionic environment. To the extent that these conditions can be met, titration to a definite value of E can be used analytically. In a titration curve, the rate of change of potential passes through a maximum and if this maximum coincides with the stoichiometric point it is merely necessary to locate the maximum; the absolute value of the potential is unimportant. This is the principal problem and its best solution is governed by a number of considerations. Neglecting for a moment the direct instrumental or manipulative methods for doing this, we may note the various end-point criteria in the order of increasing certainty. In the immediate vicinity of the end point the reagent is added dropwise or in small increments of a more dilute reagent and

1. The maximum "throw" or "kick" of the indicating element (galvanometer or meter) is sought. In much routine industrial or control work an off-scale deflection is taken, and anything more time-consuming than this is considered objectionable.
2. A mental note is taken of the maximum throw per drop, thus defining the end point to within a drop or an estimated fraction thereof.
3. Several readings of the potential are taken before and after the end point and the $\Delta E/\Delta cc$ values are tabulated. Simple inspection of the data establishes the end point with some additional opportunity to favor one value a little more than its predecessor or successor (justifiable if the curve is symmetrical).
4. A curve is plotted, preferably with $\Delta E/\Delta cc$ values as ordinates and *cc* as abscissas (*b*, Figure 146), and the exact location of the maximum is noted.

The general theory of titration curves is discussed in great detail in the texts (particularly well in *25*, *158*). Other mathematical approaches to the location or direct calculation of end points have been made by a number of investigators (*25*, *85*). These depend upon the assignment of an exact or semiempirical equation to the curve and computing the maximum. These methods have been found to predict satisfactory end points from relatively few readings.

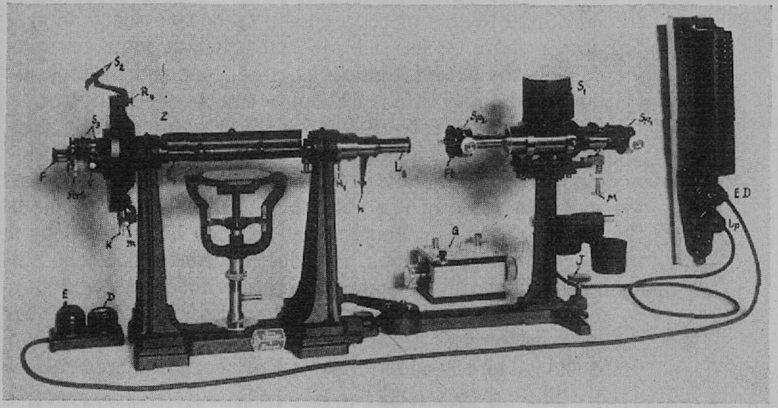
The importance of this problem cannot be overemphasized. Potentiometric titrations are so very useful and capable of



Courtesy, F. W. Zerban, New York Sugar Trade Laboratory

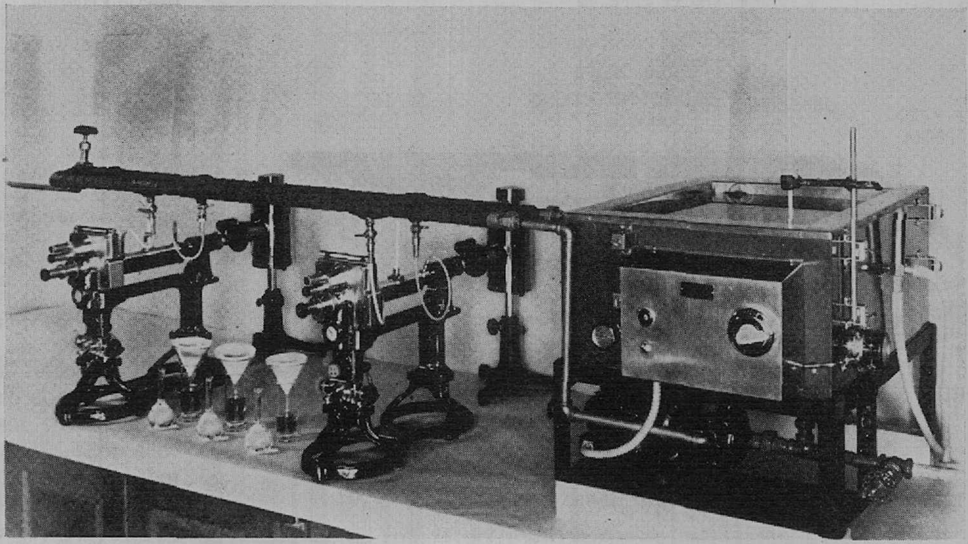
FIGURE 141. SACCHARIMETERS

(*Right to Left*). Bates double quartz wedge saccharimeter (Fric), Schmidt and Haensch double quartz wedge saccharimeters, Bausch & Lomb single quartz wedge saccharimeter. Light sources are behind an insulated wall and laboratory is kept at a constant temperature of 20° C.



Courtesy, Akatos, Inc.

FIGURE 142. SCHMIDT AND HAENSCH PRECISION POLARIMETER ASSEMBLY WITH SPECTROSCOPE-MONOCHROMATOR



Courtesy, National Bureau of Standards

FIGURE 143. CONSTANT-TEMPERATURE BATH WITH CIRCULATING PUMP AND TWO BATES SACCHARIMETERS

Water from bath is pumped through jackets of polariscope tubes

high precision that any factor which stands in the way of their more extensive use is a challenge. The research man has no aversion to curve plotting or computation—he revels in it. The person called upon to do a large volume of work would like something as striking as the color change of an indicator, yet retaining the unique and distinctive advantages of potentiometric titrations. This seems to be very largely an instrumental problem and criteria in this connection are discussed under that heading.

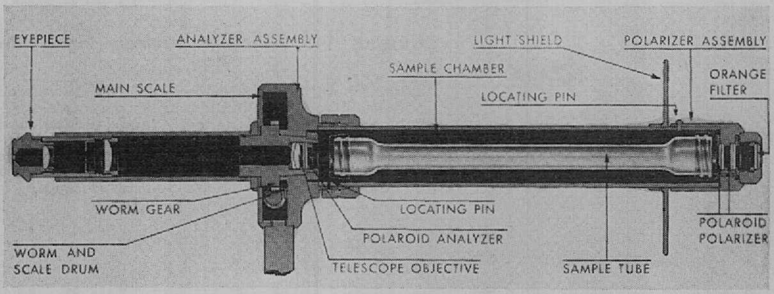
INSTRUMENTS AND APPARATUS. Individual components of potentiometric equipment have been available for many years. They are offered now in still greater variety and perfection; the participation of the radio industry in this respect is increasingly evident. Aside from equipment intended for instruction, the trend is in the direction of compact units with little or no exposed wiring. A fine example of precision equipment is shown in Figure 147, which combines the reliability of the classical potentiometer with the modern advantages of electronic detection of the condition of balance. A convenient assembly for research is shown in Figure 148.

The most striking developments are to be found in pH meters, caused largely by the need for acceptable instruments to utilize the useful properties of the glass electrode. [Instruments are manufactured by Beckman (National Technical Laboratories), Cambridge, Cameron, Coleman, Hellige, Leeds & Northrup, and Leitz and by some of these in various models—i. e., research, industrial, or recording types.] The electrode itself has grown apace and is now available in many forms and for specific applications. Examples of one manufacturer's offering are shown in Figures 149 and 150.

There is great need for a definitive treatment of modern potentiometric equipment and two critical reviews have been

Courtesy, Spencer Lens Co.

FIGURE 144. POLARIMETER UTILIZING POLAROID FILM



Courtesy, Spencer Lens Co.

FIGURE 145. SECTIONAL VIEW OF SPENCER POLARIMETER

promised for the ANALYTICAL EDITION, one on electrode systems and another on electronics. The need arises from the lack of published details of circuits and technical data on performance. There are one or two notable exceptions to this practice or oversight. All too often performance is designated in chemical rather than electrical terms and adjectively rather than numerically. It may be contended that the chemist is in general interested solely in the former, but it would seem that the minimal information should include numerical data on stability, reproducibility, sensitivity (actual, not engraved scale divisions), input resistance, battery supply voltage effects, or line-voltage variation effects.

Much of the earlier prejudice against vacuum tube devices has disappeared and under the best possible circumstances—demonstrated reliability. The use of the inverted triode or tetrode (*36*) was an important step and the extensive use of the inverse feed-back principle (*222, 272*) has opened up great possibilities for two reasons. This principle reduces the influence of tube characteristics and supply voltage variations to negligible proportions and carries with it the means of devising self-compensating circuits—that is, potentiometric balancing without moving parts. These advantages are still more apparent in automatic recording or control installations.

The principle of differential titration in its various forms involves the use of two electrodes of the same type and some mechanical means for withholding a small portion of the solution around one of the electrodes while the potential is being measured. For each addition of the reagent, small differences in potential will appear until the end point is approached, beyond which they will again diminish. Thus $\Delta E/\Delta cc$ is measured directly. This method has been brought to a high degree of perfection by MacInnes and associates (*185*). Acid solutions can be determined with a precision of 0.003 per cent. Other arrangements have been classified in Furman's review (*84*). The electrical equivalent of this principle has been demonstrated and applied to various classes of titration, using a pulse amplifier (*11*). The sole requirement was shown to be a sufficiently rapid attainment of equilibrium at the electrodes. Shenk and Fenwick (*251*) have discussed automatic titrations.

APPLICATIONS. Potentiometric methods have been applied in aqueous and nonaqueous systems and to organic and inorganic substances and most of these methods have been extended to microtechniques. The summaries by Furman (*84*) and Böttger (*25*) list all applications according to substances and class of titration. Potentiometric methods are characterized by high precision and freedom from many of the difficulties which beset the use of indicators (*136*). The question of speed depends largely upon the system—that is, the ease with which the end point can be detected. Some improvement in this factor can be expected in the future, not in the sense of justifying the use of the methods, but rather in making their extremely wide range of applicability more general.

A few typical industrial applications are included here, Figure 151 showing some measurements of pH in nonaqueous solutions. The extension of these principles to automatic recording and control is in an advanced state of development, and the engineering aspects of this technique are a

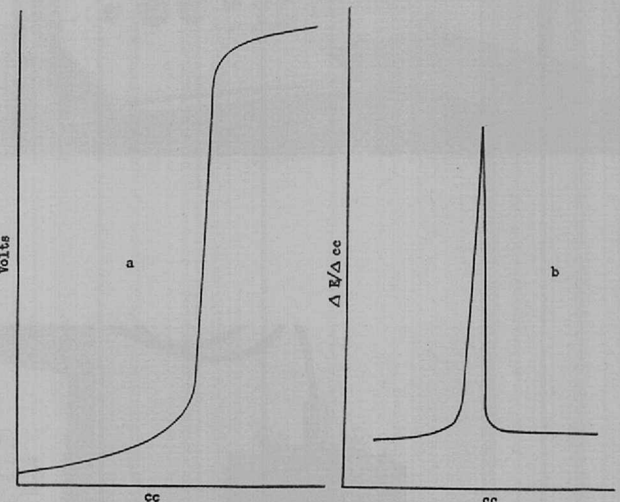


FIGURE 146. TYPICAL TITRATION CURVE

a, direct form; *b*, differential form

Courtesy, Leeds & Northrup Co.

FIGURE 147. PRECISE pH SETUP

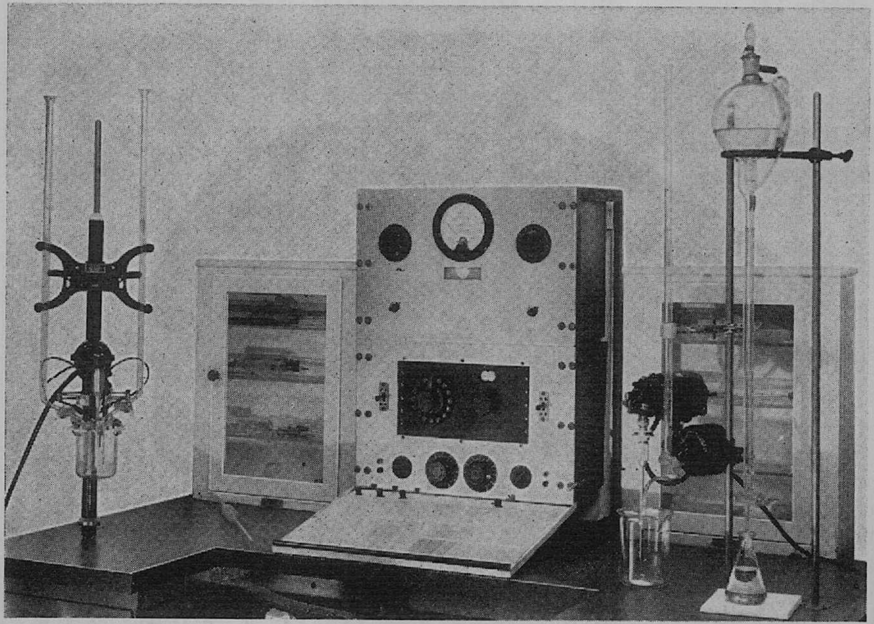


FIGURE 148. POTENTIOMETRIC-TITRATION BAY

Three separate units are available: a conventional potentiometer with illuminated lamp and scale galvanometer, electronic titrimeter (upper section), and electronic section used as vacuum tube galvanometer for standard potentiometer, if absolute values of e. m. f are required. Circuit combinations are easily selected by telephone-type switches.

Courtesy, New York University

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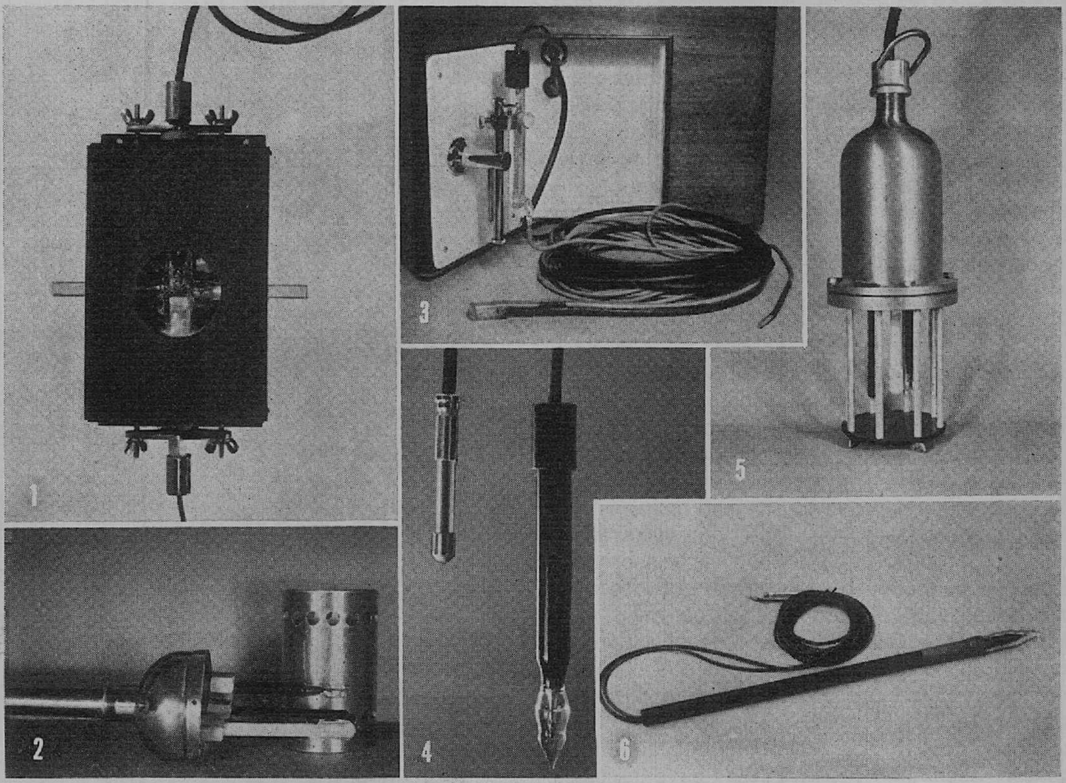
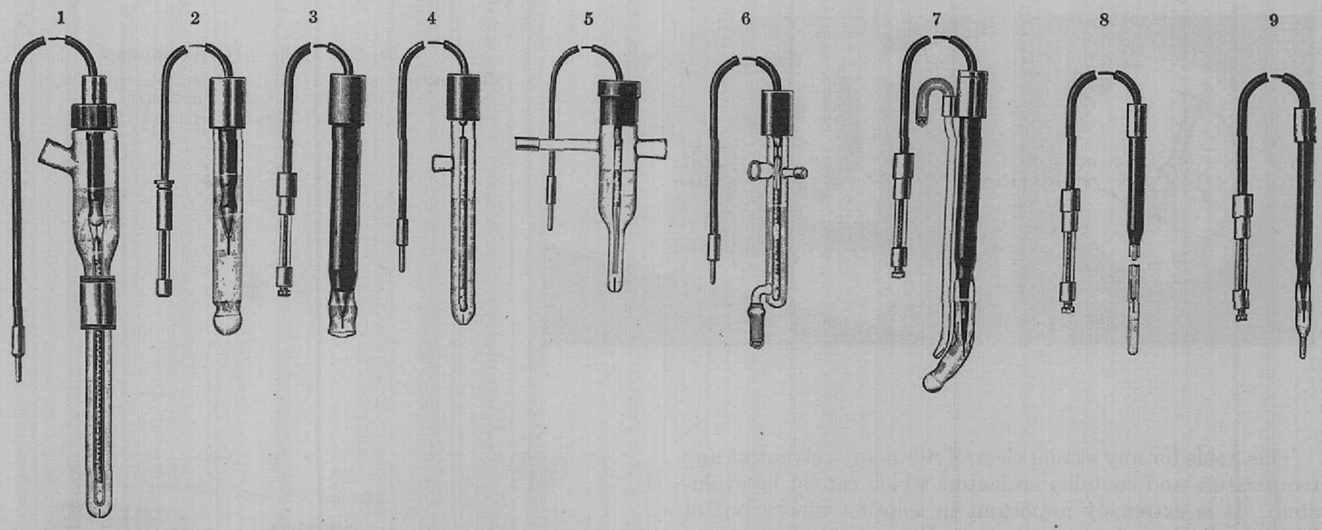


Courtesy, National Technical Laboratories

FIGURE 149. GLASS ELECTRODES

1. Flow-type electrode assembly for low flows, 50 ml. per minute. Glass and calomel electrodes mounted in Pyrex cross embedded in plaster of Paris
2. Immersion assembly with metal shield, for use in tanks and vats on solutions containing solid materials. All stainless steel
3. Glass-calomel electrode assembly for stomach pH studies *in vivo*. Glass electrode is protected by perforated Lucite head. One small rubber tube is filled with potassium chloride solution to form liquid junction, other tube is for withdrawing samples
4. Spear-type glass electrode for cheese, soil, etc. Internally shielded with integrally attached shielded lead
5. Immersion-type assembly for depths of several hundred feet in plankton studies. Glass and calomel electrodes shown with resistance thermometer. Platinum electrode may also be used for O-R studies. Assembly attached to cable
6. Glass-calomel electrode assembly for vaginal pH studies *in vivo*. Ground-glass shoulder is provided above glass electrode bulb for potassium chloride reservoir and liquid junction. Application assembly attached to Bakelite tube



Courtesy, National Technical Laboratories

Figure 150. Glass Electrodes

1. With potassium chloride reservoir, for continuous service, 0° to 100° C.
2. For continuous service, 50° to 100° C.
3. Flat membrane type for pH studies on skin and surfaces, internally shielded

4, 5. Fiber-type calomel electrodes, liquid junction through porous fiber sealed into glass ends

6. Calomel electrode, for mounting on pH meter, with potassium chloride–filled tubing connection to application fittings
7. Glass electrode for vaginal pH studies
8. Internally shielded type for cheese, etc.
9. Internally shielded type for small-animal work

subject in themselves (*197*). Two isolated examples are shown in Figure 152 and others in Figures 153 and 154.

Conductometric

Theory. Analytical applications of conductance are based on (1) empirical conductance-concentration relationship, and (2) change of conductance during a titration.

In most industrial applications, the necessary calibrations are purely empirical and presuppose that the conductance can be related to the concentration of the desired constituent in terms of some other kind of analysis. Even for a single electrolyte no equation is completely satisfactory over the entire concentration range.

Definitions. Solutions of electrolytes obey Ohm's law and the specific resistance is defined as the resistance in ohms of a 1-cm. cube. The reciprocal of this quantity is the specific conductance, K. The equivalent conductance, Λ, is given by

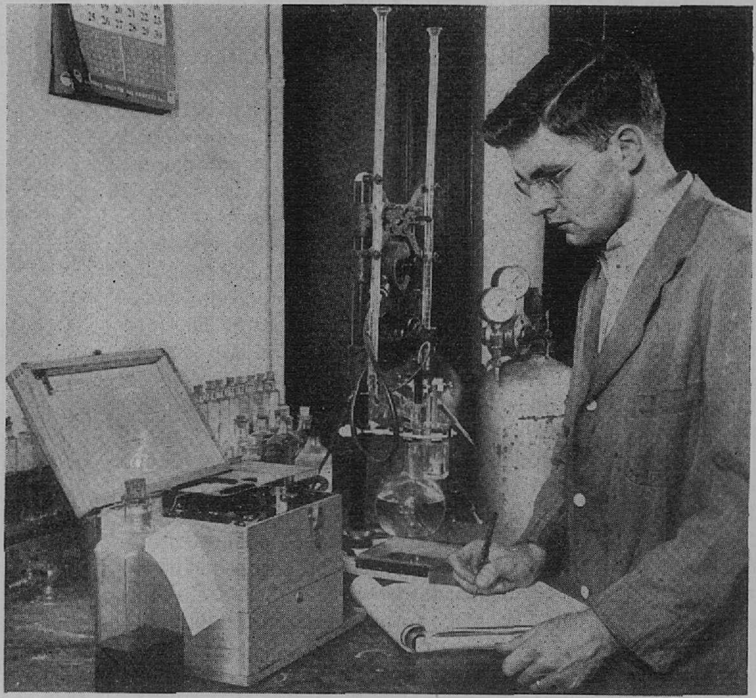
$$\Lambda = K \times \frac{1000}{c}$$

where c = concentration in equivalents per liter.

The limiting value of Λ as the concentration approaches zero is called the equivalent conductance at infinite dilution, Λ_0, and the law of Kohlrausch (*101*) states that this value is the sum of the individual ionic conductances—i. e., the sum of the anionic and cationic conductances.

Many expressions have been proposed, relating conductance to concentration (*154*). Modern theories of solution indicate that a square root law is required. For extremely dilute solutions, the equation of Onsager (*184*) expresses the equivalent conductance as

$$\Lambda = \Lambda_0 - \left[\frac{0.9834 \times 10^6}{(DT)^{3/2}} w\Lambda_0 + \frac{28.94 \quad zi}{(DT)^{1/2}\eta}\right] \sqrt{(z^+ + z^-)\,C} \quad (7)$$



Courtesy, Socony-Vacuum Oil Co. and E. Leitz, Inc.

Figure 151. Titrator with pH Equipment

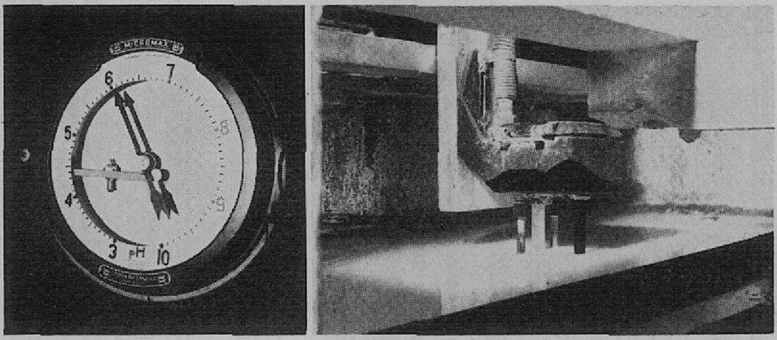
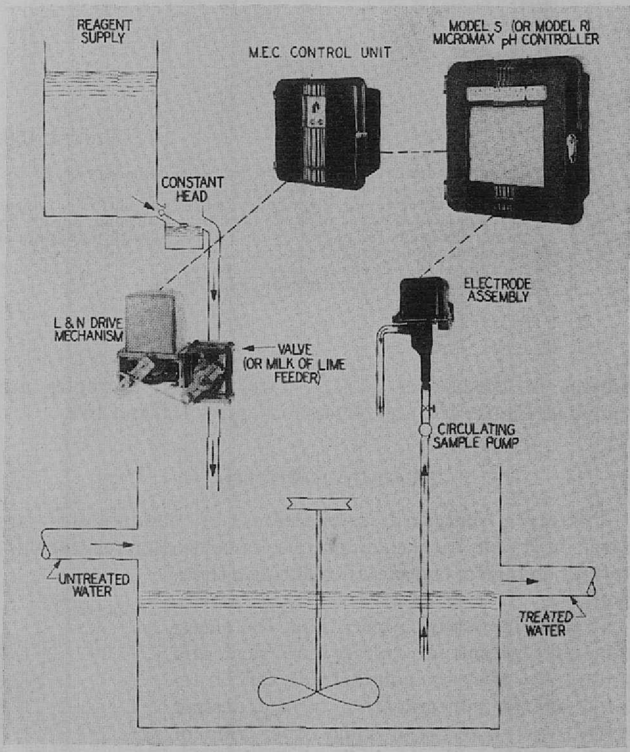


FIGURE 152. pH RECORDERS

Micromax recorder (*left*) and antimony electrode (*right*) detect pH of kaolin suspension

Courtesy, Leeds & Northrup Co.



Courtesy, Leeds & Northrup Co.

FIGURE 153. MICROMAX pH CONTROL IN REACTION TANK, USING ANTIMONY ELECTRODE

This holds for any strong electrolyte in any solvent at any temperature and contains no factors which cannot be evaluated. It is extremely important in solution theory but of little practical use for our purpose. Extension to higher concentrations requires the addition of other empirical terms and it is to be regarded as a fundamental limiting law (*184*).

The individual ionic conductances are useful and important in understanding or planning any analytical scheme. Table III (from *184*) gives the values of several of the more important ions at 25° C. The *temperature coefficient of conductance* depends upon the ion, but amounts roughly to 2 per cent per degree. This is important enough to require temperature control during the measurements, indeed to an extent fixed by the required precision. The conductance of an electrolyte depends enormously on the solvent; indirectly use can be made of this analytically—i. e., in the analysis of mixed solvents.

An important distinction from other electrical methods is to be noted, in that there is nothing characteristic or distinctive about conductance; all ionic species in the system will contribute to the total conductance. For all but the simplest systems, therefore, a titration or selective reaction with one or more kinds of ions must be employed.

Conductance titrations are based upon a measurement of the change in conductance of the solution when one or more of the ions are precipitated, removed to form slightly ionized substances (water), evolved as a gas, or tied up in the form of a complex ion. This process may be expected to cease when these ions have reacted in stoichiometric amount with the added reagent, and the subsequent addition of reagent will cause a further change in conductance, but in a different manner. An "end point" is never obtained directly in this type of titration; rather, one calculates the point at which stoichiometric equality was reached. The various classes of reactions and the course of their conductance have been discussed by Kolthoff and others (*29*, *155*, *156*), and representative examples are indicated schematically in Figure 155. The end point is obtained by the intersection of the two straight lines (*155*). For measurements of very high precision the intersection may be calculated from the equations of the two straight lines (*26*, *192*).

The method presupposes no appreciable change in volume during the course of the titration; hence, reagent concentrations are from 20 to 50 times those of the solution to be titrated and microburets are used. The need for temperature control calls for a thermostat. European practice inclines to the use of an ice bath or constant-temperature jackets built around the cell, using the vapor of a boiling pure liquid.

INSTRUMENTAL METHODS. Conductance cells are available in great variety. In principle the cell consists of two platinum plates of area and spacing dependent upon the order of magnitude of the expected conductance. The solution is contained in a glass or quartz cell between and around the electrodes, which have been made in plunge type and pipet style and in rugged pattern to be screwed into pipe lines. The platinum electrode may be bright, sand-blasted, or lightly platinized (platinum black). The relative merits of each are discussed in standard texts. In general, polarization effects are more common on bare electrodes; attainment of equilibrium is more rapid at platinized electrodes; but there are also chances for adsorption or subsequent desorption which may be troublesome in very dilute solutions. Calibration is effected by measuring accurately standardized solutions; the absolute conductance of potassium chloride solutions is known with a high degree of precision (*147*). The cell constant obtainable for such measurements is rarely of any use in titrations, but necessary in empirical conductance measurements.

The resistance of the electrolyte is usually measured with alternating current to avoid electrical as well as concentration-polarization effects. However, direct current measurements with special arrangements are equal in precision to the best alternating current results.

A simple application of Ohm's law may be used to measure the resistance of the electrolyte. If a constant alternating current potential is maintained across the cell, the current which flows will be inversely proportional to the resistance, or directly proportional to the conductance. This has some advantage in titration work. It is used in the vacuum tube arrangements of Treadwell (*277*) and Ehrhardt (*68*).

The more usual method is to use a Wheatstone bridge in which the conductance cell forms one of the arms. Since the cell is not a pure resistor but also a capacitator, perfect balance cannot be obtained in the alternating current bridge unless it is balanced for the impedance as well as the resistive components. This is usually achieved by shunting the opposite arm with a small variable capacitor.

TABLE III. LIMITING ION CONDUCTANCES AT 25° C.

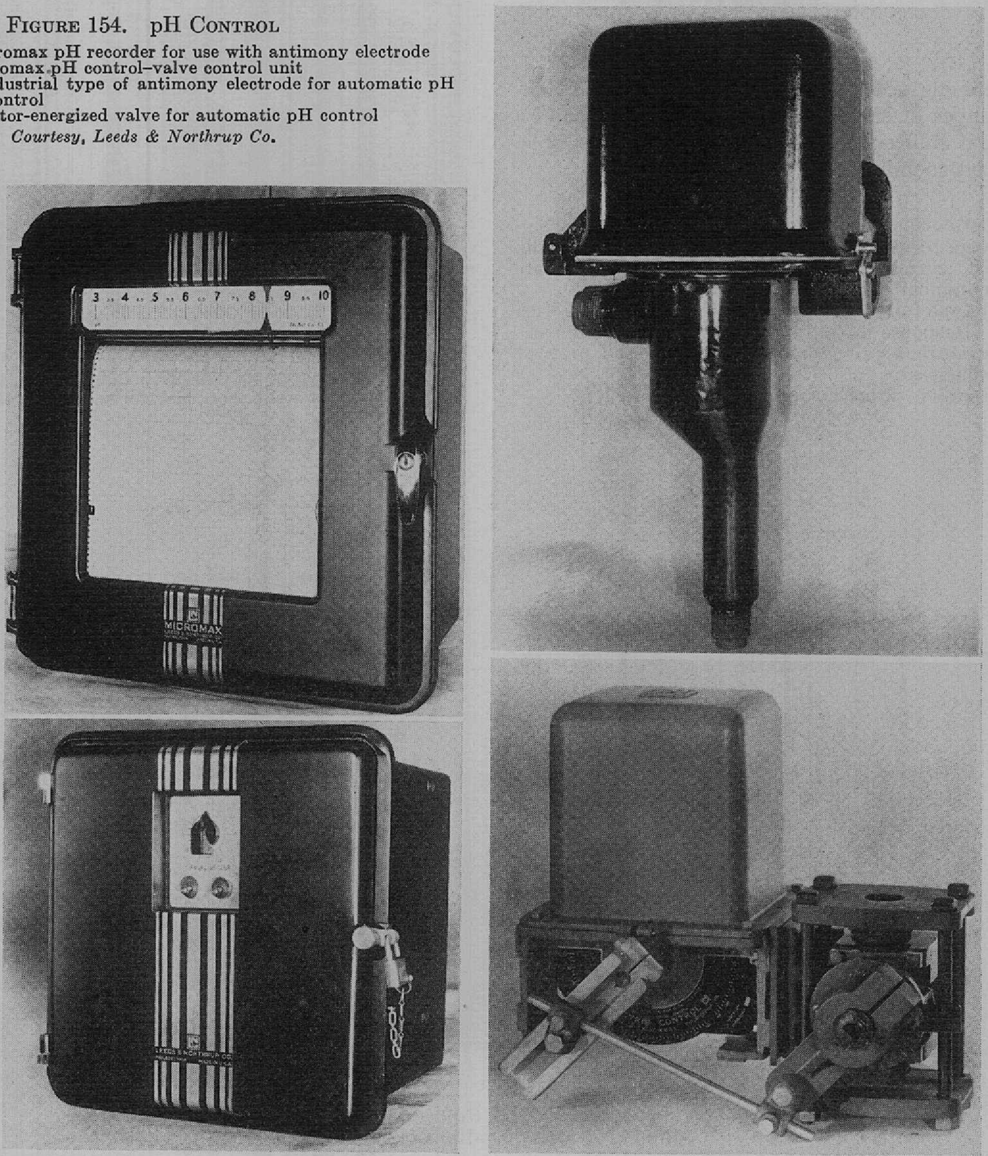
Cation	λ_0^+	Anion	λ_0^-
K^+	73.52	Cl^-	76.34
Na^+	50.11	Br^-	78.4
H^+	349.82	I^-	76.85
Ag^+	61.92	NO_3^-	71.44
Li^+	38.69	HCO_3^-	44.48
NH_4^+	73.4	OH^-	198
Tl^+	74.7	$CH_3CO_2^-$	40.9
$^1/_2\ Ca^{++}$	59.50	$CH_2ClCO_2^-$	39.7
$^1/_2\ Ba^{++}$	63.64	$CH_3CH_2CO_2^-$	35.81
$^1/_2\ Sr^{++}$	59.46	$CH_3(CH_2)_2CO_2^-$	32.59
$^1/_2\ Mg^{++}$	53.06	ClO_4^-	68.0
$^1/_3\ La^{+++}$	69.6	$C_4H_5CO_2^-$	32.3
$^1/_3\ Co(NH_3)_6$	102.3	$^1/_2\ SO_4^{--}$	79.8
....	....	$^1/_3\ Fe(CN)_6^{---}$	101.0
....	....	$^1/_4\ Fe(CN)_6^{----}$	110.5

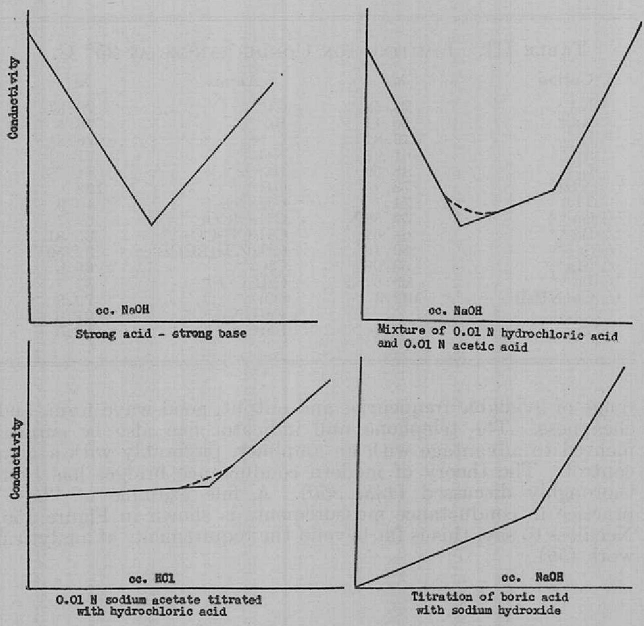
The bridge is fed with a low voltage source of alternating current. Sixty-cycle alternating current is used in commercial conductance bridges, with an alternating current galvanometer to indicate when the bridge is balanced. If a telephone receiver is used, higher frequencies must be employed, and 1000 cycles is a convenient value. In modern work, vacuum tube oscillators are used for this purpose. They are characterized by a wide range of available frequencies and output, good wave form, and cheapness. The telephone null indicator can also be supplemented to advantage with an amplifier, preferably with a gain control. The theory of modern conductance bridges has been thoroughly discussed (*148*, *250*). A fine example of "best" practice in conductance measurements is shown in Figure 156. Needless to say, this is far beyond the requirements of analytical work (*56*).

FIGURE 154. pH CONTROL

(*Upper Left*). Micromax pH recorder for use with antimony electrode
(*Lower Left*). Micromax pH control-valve control unit
(*Upper Right*). Industrial type of antimony electrode for automatic pH control
(*Lower Right*). Motor-energized valve for automatic pH control

Courtesy, Leeds & Northrup Co.





Strong acid - strong base

Mixture of 0.01 N hydrochloric acid and 0.01 N acetic acid

0.01 N sodium acetate titrated with hydrochloric acid

Titration of boric acid with sodium hydroxide

FIGURE 155. REPRESENTATIVE CONDUCTANCE TITRATION CURVES

The use of telephone receivers is not too convenient nor comfortable. A number of substitutes have been sought and a visual indicator, if sufficiently sensitive, is highly desirable. Some solutions to this problem may be mentioned.

1. Vacuum-thermocouple-galvanometer. The unbalance signal heats a fine wire to which a thermal junction is welded, developing a direct current voltage. The disadvantages are thermal lag and nonlinear response (square law, RI^2).
2. Instrument-type full-wave copper oxide rectifier used with a galvanometer. Response instantaneous (rectifier), nonlinear.
3. Alternating current galvanometers, can be used only at relatively low frequencies.
4. Amplifier-rectifier, direct current meter.
5. Special bridge-balance indicators (electronic) available in great variety. The most ingenious solution seems to be that of Garman (*86, 87*). With one tube, or in the later model two tubes, a close approximation to the perfect bridge-balance indicator is obtained. The meter deflection is down scale, making damage impossible, and the sensitivity reaches a maximum at zero signal.

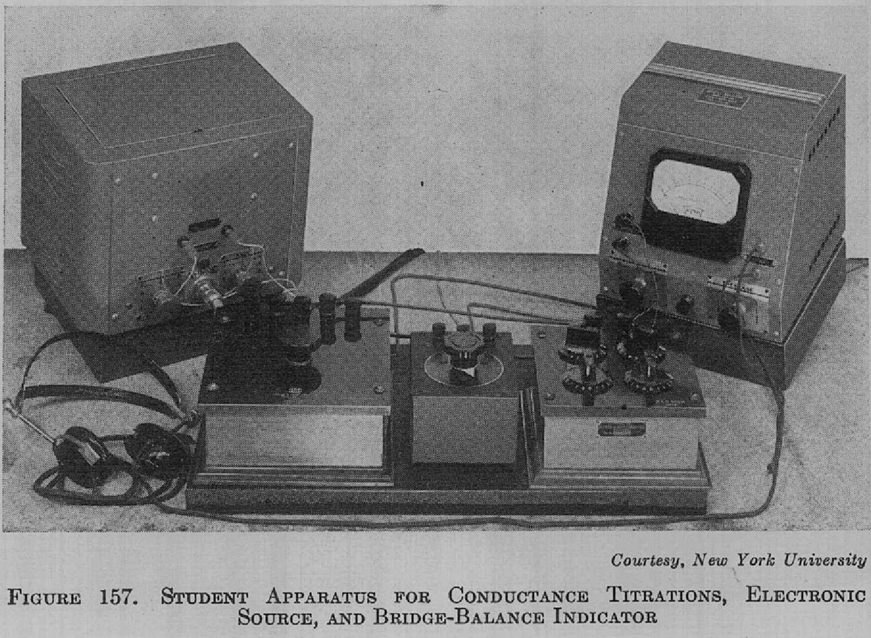
Figure 157 illustrates a typical installation for student use.

The compact unit on the left is the vacuum tube oscillator with controllable output, the one on the right is the Garman bridge-balance indicator. The unit in the foreground contains

Courtesy, Leeds & Northrup Co.

FIGURE 156. HIGH-PRECISION CONDUCTANCE ASSEMBLY

Jones bridge, vacuum tube oscillator, output amplifier, Mueller bridge for temperature measurements, and thermostat regulating to ±0.001° C.



Courtesy, New York University

FIGURE 157. STUDENT APPARATUS FOR CONDUCTANCE TITRATIONS, ELECTRONIC SOURCE, AND BRIDGE-BALANCE INDICATOR

a decade resistance box, Kohlrausch slide wire, and Wagner ground. The wiring in the bridge circuit is all exposed; the student makes these connections. Each bridge assembly is plugged into a wall socket, leads from which pass through shielded pipe to the main laboratory thermostat. Similar "station" outlets at the thermostat enable the student to connect his conductance cell to his own bridge circuit.

A complete installation for research purposes is shown in Figure 158.

It is assembled entirely from standard, interchangeable radio equipment including the relay-rack panels. The lower unit contains the oscillator with a choice of three frequencies, 400, 1000, and 2000 cycles, with controllable output. The midsection contains a ratio-arm box and five decade resistor units (both General Radio Co.). No slide wire is used in this bridge. In addition, this unit houses the compensating condenser and the Wagner-ground network. The upper section contains the Garman bridge-balance indicator. The entire instrument is mounted on the wall at a convenient height for the operator. Shielded cable connects with the conductance cell in an adjacent thyratron-controlled oil thermostat (not shown).

The advantages of the newer methods in conductance technique are emphasized by Jander and Pfundt (*25*, *141*). They show that present practice permits the analysis of a substance in the presence of a five hundredfold excess of indifferent electrolytes, and that the recent method for determining as little as 0.04 microgram of arsenic is wholly out of the question with the old-fashioned slide wire–telephone arrangement.

APPLICATIONS. 1. *Direct Measurement of Conductance.* Applications of this class are summarized by Sandera (*238*) with an extensive bibliography of 274 references. To select a dozen at random and indicate the wide range of applicability: conductance measurements have been found useful in determining nitric acid in plant control (*46*), hardiness of winter wheats (*286*), mineral content of wines (*70*), neutralizers in dairy products (*50*), adulteration in maple sirup (*45*), priming of boiler water and condenser leakage (*282*), purity of water supplies (*101*), carbon dioxide and other gases in botanical investigations (*207*), pan boiling control in the sugar industry (*17*), automatic analysis of sulfur dioxide in industrial gases (*78*, *193*), properties of yarns and fabrics (*53*), and condition of pork and bacon (*12*).

Among the well-established applications is sugar ash determination, which has largely replaced the tedious gravimetric procedure. The method has been the subject of many investigations (*180*, *312*, *313*). Figure 159 illustrates the installation of equipment for this purpose in the laboratory of an eminent authority in the sugar field.

Another application is illustrated in Figure 160, primarily because this measurement requires auxiliary equipment peculiar to the nature of the sample. A U. S. Department of Agriculture bulletin (*284*) contains official data and tables for converting the readings of this instrument into the moisture content of typical grains and cereals. The same instrument may be used with a special electrode for determining the moisture content of lumber (see also *265*).

CONDUCTANCE TITRATIONS. Jander and Pfundt (*25*, Vol. II) summarize the work that has been done on 96 important substances, listing 207 references. This compilation is in convenient tabular form, including useful comments on other applications of the method, special precautions, possible interferences, and estimates of precision or reliability. In this list, in addition to the titration of the commoner inorganic ions, are to be found methods for the analysis of alkaloids, amino acids, aniline, chlorophenols, dimethylamine, fatty acids, tannins, isovanillin, creatine, lactic acid, naphthol, phenol, pyridine, salicylates, thymol, etc.

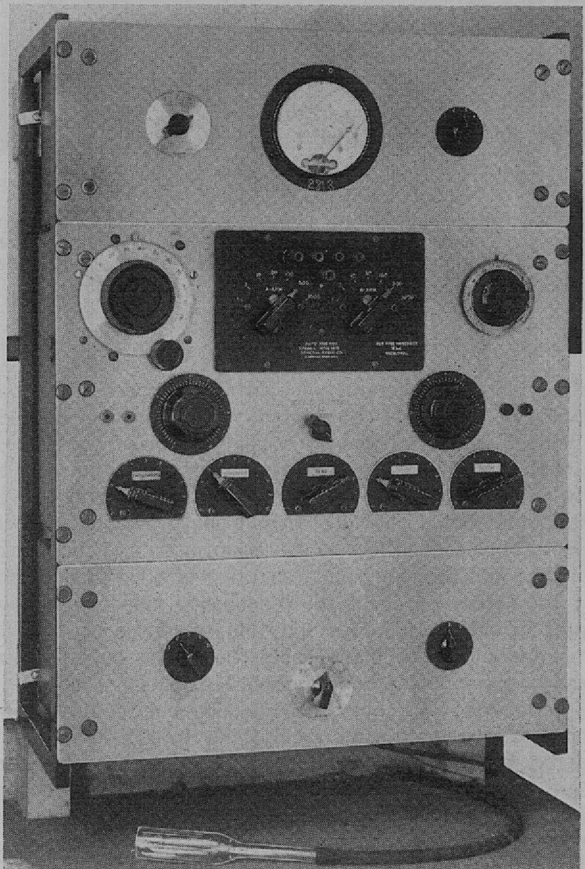
In a supplementary listing, devoted mostly to microdeterminations (*25*), Jander and Pfundt indicate the improvements which have resulted from modern techniques. The following examples give the minimal quantities analyzed (in micrograms, 10^{-6} gram), the volume of solution, and the precision obtainable: arsenic 0.04 to 100 γ, 3 to 4 cc., ± 10 per cent; lead 1–2 γ, 3 to 4 cc., ±7 per cent; cadmium 1 γ, 3 to 4 cc., ±10 per cent; copper 1 γ, 3 to 4 cc., ±5 per cent; silver 1 γ, 3 to 4 cc., ±5 to 10 per cent; bismuth 10 γ, 3 to 4 cc., ±7 per cent.

The precision which can be expected in a representative conductance titration may be inferred from Table IV, which compares analyses of solutions of technical ammonium sulfate with the gravimetrically determined values. The conductance titrations were made at room temperature after the addition of alcohol.

TABLE IV. CONDUCTANCE TITRATIONS OF TECHNICAL AMMONIUM SULFATE SOLUTIONS (*215*)

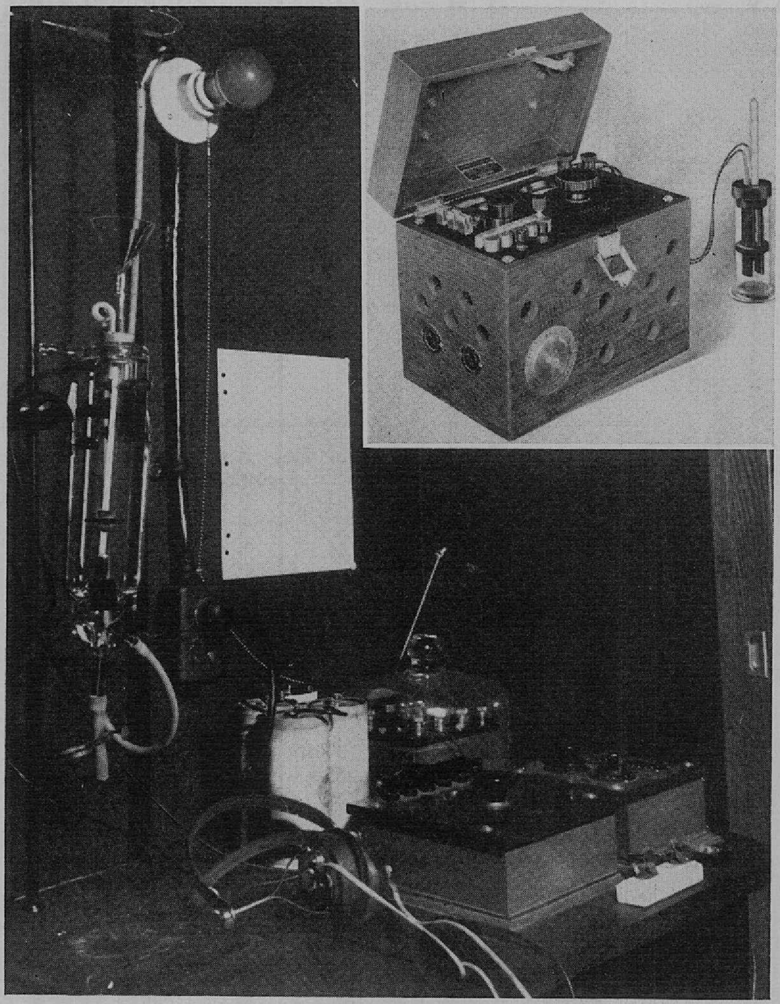
Sample No.	SO_3 Conductometric %	SO_3 Gravimetric %	Sample No.	SO_3 Conductometric %	SO_3 Gravimetric %
31	21.05	21.12	40	24.35	24.35
32	20.44	20.49	41	22.64	22.68
33	21.86	21.90	42	21.40	21.53
34	20.82	20.88	43	22.30	22.36
35	22.06	22.13	44	22.56	22.62
36	21.60	21.64	45	19.70	19.60
37	20.62	20.64	46	22.86	22.90
38	21.26	21.34	47	18.69	18.63
39	22.49	22.47	48	22.45	22.45

Values signify grams of SO_3 per 100 cc.



Courtesy, New York University

FIGURE 158. CONDUCTANCE APPARATUS WITH ELECTRONIC SOURCE OF ALTERNATING CURRENT AND ELECTRONIC BRIDGE-BALANCE INDICATOR



Courtesy, F. W. Zerban, New York Sugar Trade Laboratory

FIGURE 159. ELECTRICAL CONDUCTIVITY APPARATUS FOR SUGAR ASH DETERMINATIONS IN A CONSTANT-TEMPERATURE ROOM (20° C.)
(*Upper Right*) SUGAR ASH BRIDGE. *Courtesy Leeds & Northrup Co.*

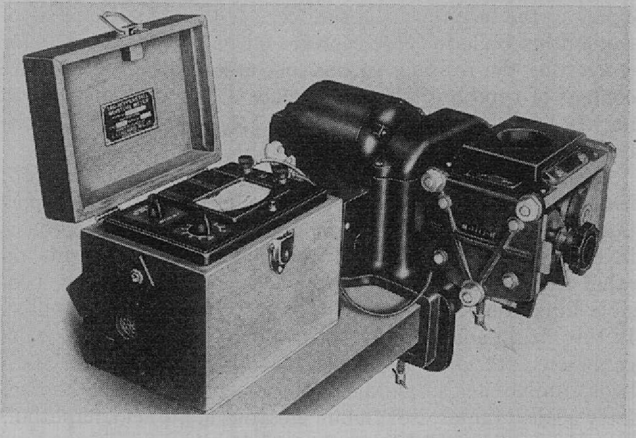
The precision of conductance titrations is generally given as 0.5 to 1 per cent, but this is really no criterion of the technique itself, since conductance measurements can be made to better than 0.01 per cent. To attain this precision would require many refinements in the volumetric technique and excellent temperature control. In addition, titrations involving precipitations are subject to sources of error not found with titrations in which no solid separates (*184*). These errors may arise from coprecipitation, occlusion, adsorption, slowness of formation of the precipitation, or conductance by the suspended solid. In many cases, the errors may be minimized by precipitating in the presence of alcohol.

CONCLUSIONS. Conductance measurements have been applied to a wide variety of analytical problems and there is an extensive literature on the subject. Empirical conductance-concentration relationships have many uses in control analyses and are well suited to automatic recording or control. Conductance titrations are particularly useful in turbid or highly colored solutions or in very dilute solutions. The "end point" is not detected in the ordinary sense of the term, but is found by a graphic or computational treatment of the conductance–reagent volume data. This is, perhaps, the main reason for the relatively unpopular status of this important method. Apparatus of any required precision is available and developments have been very rapid, particularly in the newer electronic instruments. There is no need for more precise measuring equipment. The only possible advantage to be derived from newer instruments is to seek some means for evaluating the end point. The computation of this value is the only bottleneck in an otherwise well-established and esteemed technique.

Electrolytic

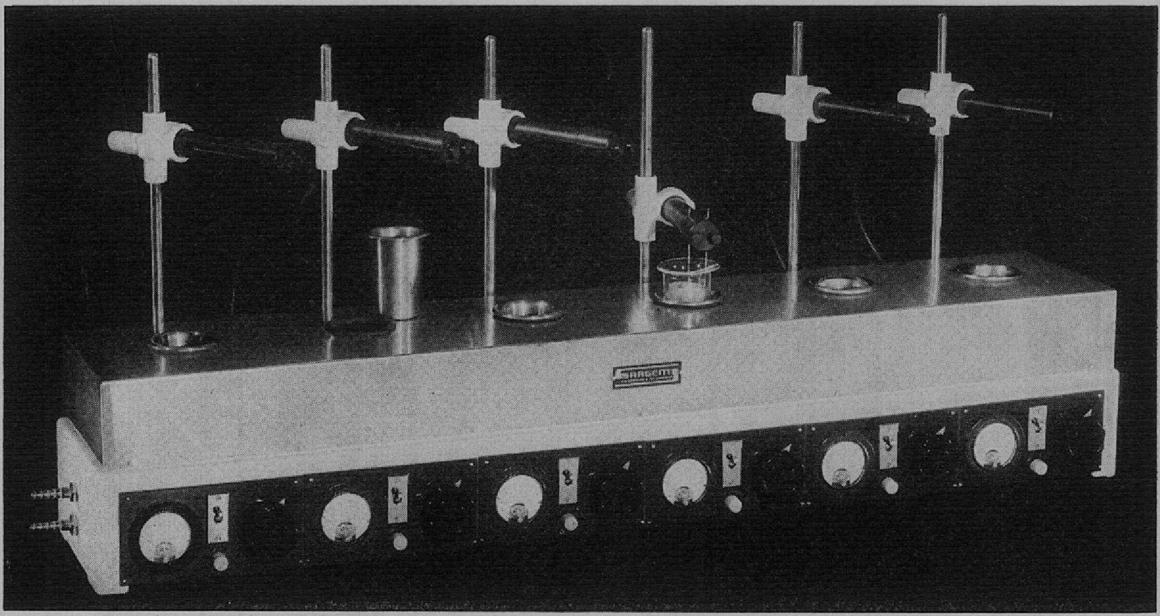
This technique is primarily an adjunct to gravimetric analysis and not an instrumental method in itself, although it seems to have possibilities in this direction. The selective electrodeposition of metals has been practiced for a long time and the foundations of the subject as a distinct means of analysis were largely due to the labors of Classen (*43*) and in this country by Smith (*258*), who was responsible for the introduction of the rotating anode and the mercury cathode (see also *74*). Detailed procedures were developed for a large number of substances and many effective means of electrolytic separation were developed. The method is still widely used, but since its inception the attention of analysts has been directed more to other electrochemical methods such as potentiometric and conductometric titrations, and analysis with the dropping mercury electrode. The subject is discussed here for the purpose of clarifying its relationship to the other techniques.

THEORY. The method is based on the fact that on applying an appropriate difference of potential between two platinum electrodes one can quantitatively deposit metals on one of the electrodes in a form suitable for direct weighing. The character of the deposit is governed by the current density, agitation of the electrolyte, and the possi-



Courtesy, C. J. Tagliabue Co.

FIGURE 160. CONDUCTANCE-TYPE TAG-HEPPENSTALL MOISTURE METER



Courtesy, E. H. Sargent & Co.

FIGURE 161. MODERN HIGH-SPEED MULTIPLE-UNIT ELECTRODEPOSITION APPARATUS, USING ELECTROMAGNETIC STIRRING

bility of codeposition of hydrogen or other metals. The purity of the deposit and its freedom from other metals depend on the relative electrode potentials, and to a large extent the possibilities of codeposition can be avoided by applying their correct potential difference and by a suitable choice of electrolyte. As electrolyte the solution may be acid or alkaline or in the form of complexes such as tartrates, citrates, or cyanides. Most metals are deposited on the cathode, although some, such as lead, are conveniently deposited as the hydrated oxide on the anode. Occasionally a mercury cathode is used on which the metal may be deposited, including the alkalies.

Theoretically the time of deposition can be calculated from Faraday's law, so that as electrolysis is carried out with a definite current the time for complete deposition should be computable. Complications arise which make this impractical, the limitations being due to diffusion effects, a lower rate of deposition toward the end of the process, and a codeposition (hydrogen). Were it not for these complications one might dispense with the final weighing of the deposit and simply calculate the weight of the deposit in terms of the total number of coulombs which were required for complete deposition. The converse process—namely, electrolytic stripping of a deposit under very carefully controlled conditions—seems to have possibilities for a completely automatic electroanalysis involving no weighing (*199*). It is altogether likely that this procedure would have to be limited to relatively simple systems.

Recent developments include the use of microtechniques and the determination of extremely small amounts of metals. The method of internal electrolysis, developed largely by Sand, has many advantages and, as the term implies, requires no applied potential, the latter being supplied by the differences of potential of two suitable electrodes immersed in the electrolyte (*42*).

INSTRUMENTS. Instrumental developments have been mostly in the direction of making these operations more rapid and convenient.

For example, in the instrument shown in Figure 161 the necessity for mechanical stirring of the electrolyte has been avoided by mounting the beaker in a stainless steel vessel which is surrounded by a large solenoid. A strong magnetic field created by the solenoid will cause rapid rotation of the electrolyte when current passes between the electrodes. This is a modernization of the principle developed many years ago by Frary. Provision is also made in this instrument for water cooling and thus appropriate temperature control of the electrolyte. The electrode holders are also greatly improved and provide for automatic alignment with the electrolysis vessel. The electrical controls are all very conveniently mounted for monitoring the applied voltage and electrolyzing current.

Another example of modern equipment is shown in Figure 162, which is entirely alternating current–operated and uses a dry rectifier and filtering circuit to provide direct current for the electrolysis. The necessary meters for current and voltage are provided, and the motor stirrer is very conveniently raised and lowered. These improvements have all assisted in obtaining rapid and accurate analyses. A collection of improved procedures has been published by Slomin (*255*).

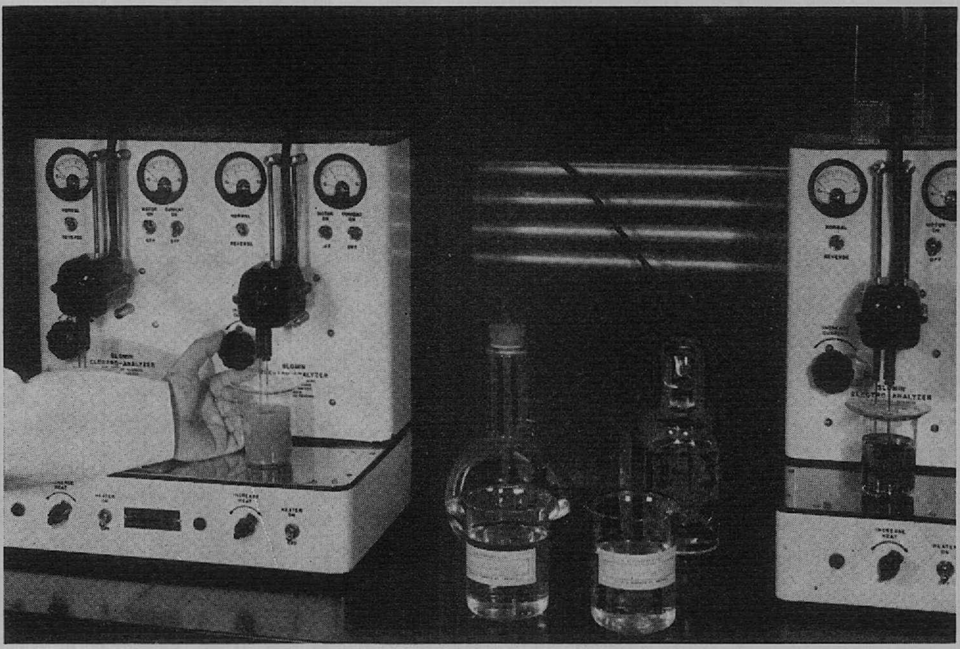
Among the micromethods the electrode system of Clarke and Hermance, Figure 163, has contributed greatly to the accuracy and convenience with which small amounts of metals can be determined. One of these, *B*, is particularly suited for the electrolysis of traces of material in very large volumes of solution.

A micro application primarily for qualitative identification consists of a minute Bakelite capsule with two platinum wires molded into the base. If, for example, a trace of copper is sought it may be plated on one of these tiny electrodes and its presence established by microscopic examination, after which it may be removed and subjected to other microchemical tests.

An example of electroanalyses in routine work is shown in Figure 164.

Polarography

This important technique is now twenty years old and is based upon the pioneer work of Jaroslav Heyrovský of Prague. The recent appearance of an excellent monograph on this subject by Kolthoff and Lingane (*161*), the first in the English language, should mark the end of the unaccountable "incubation" period which this subject has undergone in



Courtesy, E. H. Sargent & Co.

FIGURE 162. SLOMIN ELECTROLYTIC ANALYZER

Smooth, stepless adjustment of voltage is made by Variac transformer, making use of rheostats unnecessary. Only a single knob adjustment is necessary to cover entire voltage range.

America. Several recent reviews are also available (*124*, *126*, *160*, *195*), and a complete bibliography (1922 to 1941) of 699 references with titles and author and subject index has been compiled by E. H. Sargent & Company (*239*). These sources provide a complete up-to-date survey in English.

Polarography is based upon the interpretation of current-voltage curves obtained by electrolyzing a solution containing electroreducible or electrooxidizable substances between electrodes, one of which is a dropping mercury electrode and the other a nonpolarizable pool of mercury or any other suitable reference electrode. Under suitable conditions, both qualitative identification and quantitative estimation can be made in one operation. Many organic substances and most inorganic ions can be determined in concentrations ranging from 10^{-6} to 10^{-2} molar. There is no destruction of the sample and it may be used, virtually unchanged, for other studies. Useful information may be obtained with the simplest equipment, but for precise or routine work several elegant instruments are commercially available. These may be manually operated or completely automatic, and with the latter complete "polarograms" may be filed away for future reference.

THEORY. We may discuss the fundamental laws by reference to a typical series of current-voltage curves shown in Figure 165.

The three curves at the right were obtained from solutions containing 0.1 M potassium chloride as supporting electrolyte and cadmium ion in concentrations of 5×10^{-4}, 1.0×10^{-3}, and 2.0×10^{-3} molar, respectively. As the applied voltage is increased no appreciable current flows until about -0.5 volt is reached (the negative sign indicates that the dropping mercury electrode is the cathode). The current then rises rapidly and at higher potentials levels off to a more or less constant value. The height of this plateau above the base line (curve for potassium chloride alone) is called the "wave height" and is a measure of the "diffusion current." The wave height is proportional to the concentration of the electroreducible ion (Cd^{++}). This is shown by the cross-plot on the left, where the increase in current (increment) is plotted against concentration. The vertical dotted line intersects each curve at a point which is equal to one half the wave height. It has a value which is common to all three curves and identifies the ion as cadmium. It is called the half-wave potential and in this case has the value -0.597 volt.

The value for the current at any time, t, during the life of the mercury drop can be expressed quantitatively by an equation derived by Ilcovic (*138*).

$$i_t = 0.732\, nFD^{1/2}Cm^{2/3}t^{1/6} \tag{8}$$

where i_t = current in amperes at time t
n = charge on the ion (valence)
F = Faraday (96,500 coulombs)
D = diffusion coefficient of ion in sq. cm. per sec.$^{-1}$
C = concentration in moles per cc.
m = weight in grams of mercury flowing from capillary per second
t = dropping time in second

A somewhat more useful form expresses i in microamperes, m in mg. per second, and concentration in millimoles per liter. Introducing the numerical value of F, Equation 8 becomes

$$i_t = 706\, nD^{1/2}Cm^{2/3}t^{1/6} \tag{9}$$

The rise in current during the life of the drop follows a curve which is a sixth-order parabola. That it truly follows Equation 8 was proved by Ilcovic by using a fast, short-period galvanometer.

It can be shown (*161*) that the average current during the life of the drop is given by

$$i_a = 605\, nD^{1/2}Cm^{2/3}t^{1/6}_{\text{max.}} \tag{10}$$

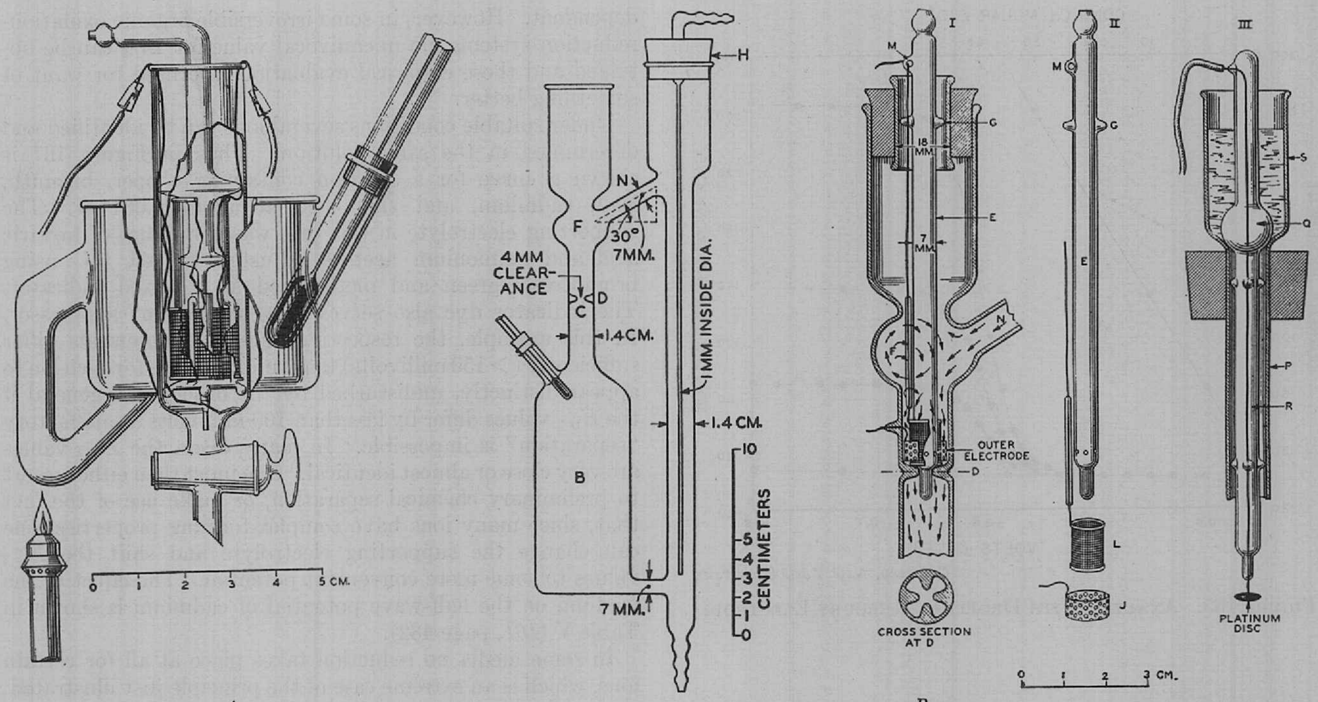
and the maximum current, at the instant the drop falls, by

$$i_{\text{max.}} = 706\, nD^{1/2}Cm^{2/3}t^{1/6} \tag{11}$$

from which it is seen that

$$i_a = 6/7\; i_{\text{max.}} \tag{12}$$

It is apparent from Equations 10 and 11 that the maximum current as well as the true average current is proportional to the concentration of the electroreducible or oxidizable substance.



A

B

Courtesy, B. L. Clarke, Bell Telephone Laboratories

FIGURE 163. MICROELECTROLYTIC CELLS

A. For small volumes
B. For large volumes

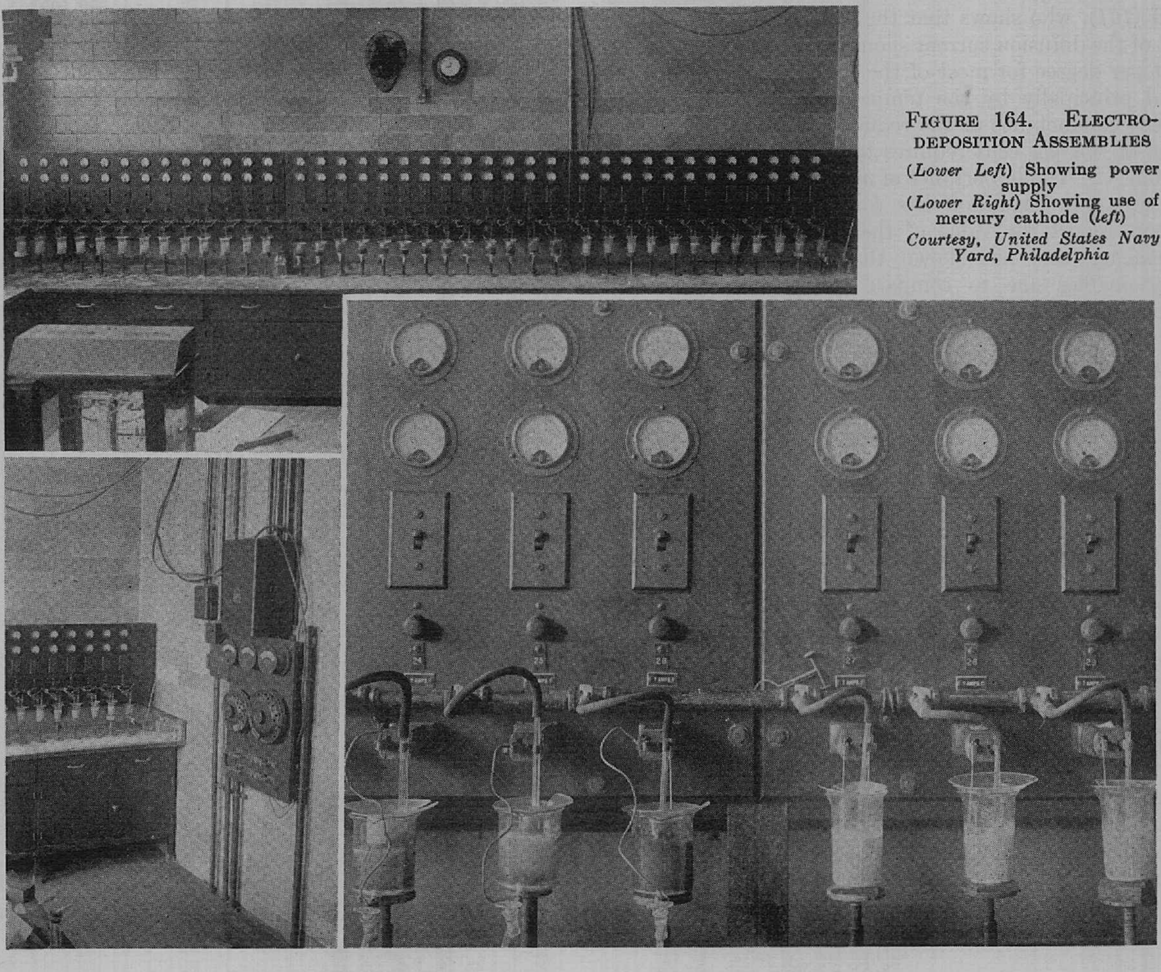
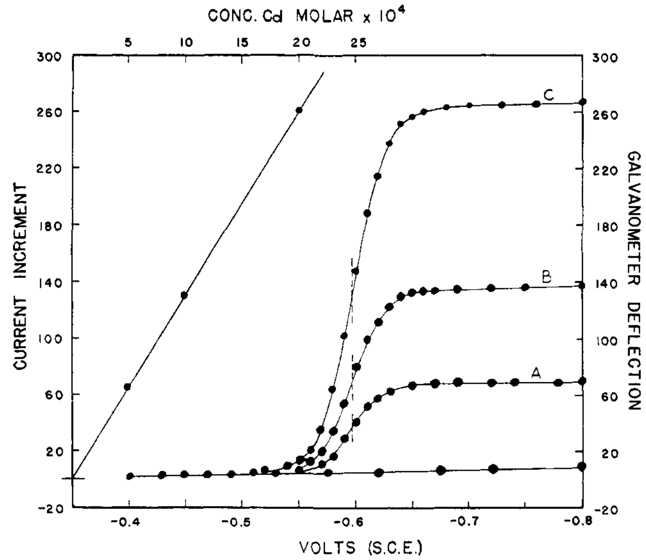


FIGURE 164. ELECTRODEPOSITION ASSEMBLIES

(*Lower Left*) Showing power supply
(*Lower Right*) Showing use of mercury cathode (*left*)
Courtesy, United States Navy Yard, Philadelphia



Courtesy, New York University

FIGURE 165. ANALYSIS WITH DROPPING MERCURY ELECTRODE

These equations have been verified by experiment in all details and are given here to emphasize the factors which must be considered in practice. For satisfactory analytical results, the dropping rate, mass of the mercury drops, and temperature must be controlled. The temperature is involved in these equations in every term except n, including the numerical constant. A complete discussion of this point is given by Kolthoff (*161*), who shows that the over-all temperature coefficient of the diffusion current should be between 1.3 and 1.6 per cent per degree for most of the common ions, and is determined principally by the temperature coefficient of the equivalent conductance of the reducible ion. In practice, a precision of ±1 per cent requires temperature control to at least ±0.5° C. The importance of m and t is evident from the Ilcovic equation. Kolthoff has recommended that all investigators report the value of the product $m^{2/3}t^{1/6}$ in the measurements, and has shown that a knowledge of this quantity enables one to compare results obtained under widely different conditions (*161*, page 61).

The concept of half-wave potential, which defines and identifies the substance, is contained in the equation developed by Heyrovský and Ilcovic (*125*).

$$E = E_{1/2} - \frac{RT}{nF} \log \frac{i}{i_d - i} \qquad (13)$$

where i represents the current for an applied potential E, and i_d the maximum value of the diffusion current at the top of the wave. In Figure 166 the dotted line indicates a current-voltage curve for Cd^{++}. The solid line shows these values recalculated and plotted, with $\log i/(i_d - i)$ as ordinates and E values as abscissas. A straight line results, as required by Equation 13, and the value of E for which $\log i/(i_d - i)$ is zero is $E_{1/2}$, the half-wave potential. In this case the value is −0.597 volt. The slope of this line should be equal to nF/RT.

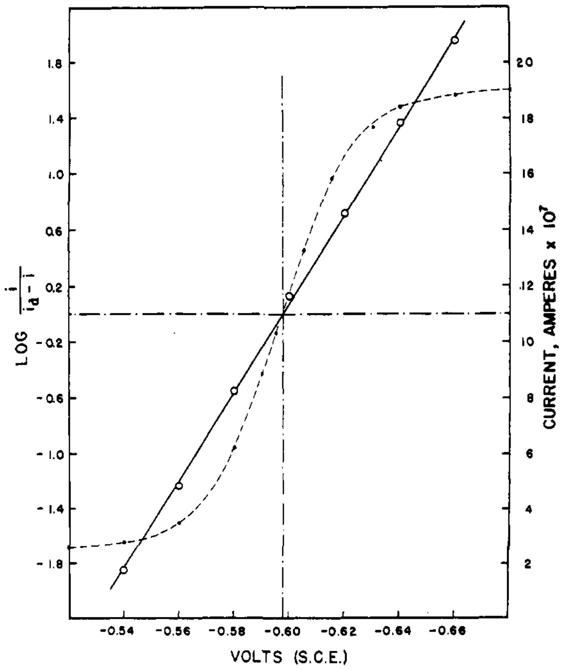
The $E_{1/2}$ value is thus seen to be independent of the concentration and marks the true inflection point of the curve, because the second derivative of E with respect to i, in the above equation, is zero. The use of $E_{1/2}$ has supplanted the older practice of drawing 45° or 35°16′ tangents to the foot of the current voltage curve, because such values are concentration-dependent. However, in some irreversible organic oxidation-reduction systems, no unequivocal value for $E_{1/2}$ can be obtained and these empirical evaluations are used for want of something better.

Under suitable conditions several ions can be identified and determined in the same solution. Thus in Figure 167 is shown a curve for a solution containing copper, bismuth, lead, cadmium, and zinc each at about 0.001 N. The supporting electrolyte in this case was a mixture of tartaric acid and ammonium acetate adjusted to pH 5.1, using bromocresol green and methyl red as a mixed indicator. The indicator dye also serves as a "maximum" suppressor. In this example, the respective half-wave potentials differ sufficiently (>150 millivolts) to permit the wave for each ion to appear distinctly, undisturbed by the others. In general if the $E_{1/2}$ values differ by less than 100 millivolts a satisfactory "separation" is impossible. In many cases, the $E_{1/2}$ values are very close or almost identical. One must then either resort to preliminary chemical separation, or make use of the fact that, since many ions have complex-forming properties, one can change the supporting electrolyte and shift the $E_{1/2}$ values to some more convenient potential. The effect of the medium on the half-wave potential of cadmium is shown in Table V (*161*, page 482).

In some media no reduction takes place at all for certain ions, which is an extreme case of the principle just illustrated.

TABLE V. EFFECT OF MEDIUM

Supporting Electrolyte	$E_{1/2}$ *vs.* Saturated Calomel Electrode
1 N KNO_3, HNO_3, or H_2SO_4	−0.586
1 N KCl or HCl	−0.642
0.1 N KCl or HCl	−0.599
1 N KI	−0.74
0.5 M neutral tartrate solution	−0.80
1 N KCN	−1.18
1 N NH_4OH + 1 N NH_4Cl	−0.75



Courtesy, New York University

FIGURE 166. EXPERIMENTAL VERIFICATION OF EQUATION 13 AND EVALUATION OF $E_{1/2}$

Considering an actual case arising in the analysis of alloys (*135*), it was found that in an ammoniacal solution containing copper, zinc, and nickel a polarogram indicated the copper as a distinct wave, but nickel and zinc appeared together—i. e., their $E_{1/2}$ values did not differ sufficiently—and the curve therefore yielded copper and the sum of the zinc and nickel. By adding an excess of cyanide, in which copper and zinc do not produce a wave, a second polarogram gave nickel alone. (It was necessary to add an excess of sulfite before the cyanide, in order to avoid the formation of cyanate.)

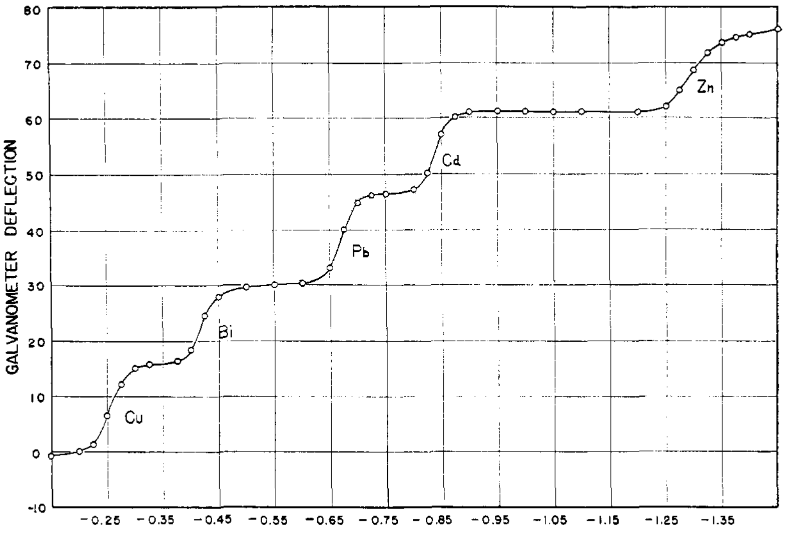
Air must be removed from the solutions, since oxygen is electroreducible at two potentials (−0.1 volt, $O_2 \rightarrow H_2O_2$ and −0.3 volt, $H_2O_2 \rightarrow H_2O$). It is evident that oxygen can be determined at these potentials. Removal of the air may be effected by a stream of pure hydrogen or nitrogen, or in some cases by illuminating gas. Sulfites are often used for this purpose.

In many cases, the current-voltage curve indicates a peculiar type of distortion characterized by a sharp initial rise of the current, which at slightly higher voltages drops back to the normal value. These maxima are highly reproducible. Although they are a nuisance in practical work, they are easily eliminated in most cases by the addition of readily adsorbable dyes, gelatin, glue, etc. Actual use of these maxima has been made in a number of cases, by measuring the progressive decrease in the height of the maximum as increasing amounts of suppressant are added. Thus, minute amounts of starch can be measured by determining the suppression of the maximum obtained in an alkaline cobalt buffer solution. A large amount of work has been done in an effort to elucidate the phenomenon, but many of its aspects are still obscure (*161*).

For the analyst's purpose, all the pertinent, fundamental points have been established and the theory has been checked in all important details by experiment.

INSTRUMENTS. Satisfactory measurements can be made on a setup assembled from commonly available electrical instruments. A simple voltage divider or potentiometer providing a range of 0 to 3 volts, preferably in three steps, in which differences as little as 5 millivolts can be selected, will serve to apply the potential to the electrode system. A galvanometer is connected in series with the source of potential and the electrodes. A Universal or Ayrton shunt for the galvanometer is necessary because the currents to be measured may range over two or three orders of magnitude (10^{-7} to 10^{-4} ampere). The use of a heavy-duty reference electrode (saturated calomel cell) is becoming increasingly popular, but if the potential is to be measured between the dropping mercury electrode and the stationary pool of mercury, means of switching over to a definite reference electrode is advisable, in order that the anode potential may be checked. The calibration and determination of current sensitivity shunt ratios, etc., follow standard electrical practice (*161*).

Manual. For routine work, a compact, self-contained, and well-designed instrument is to be preferred. Several excellent instruments are commercially available, both in the manual and automatically recording form. A typical example of the manually operated type is shown in Figures 168 and 169 and is based on preliminary development work by the writer (*75*).



Courtesy, New York University

FIGURE 167. CURRENT VOLTAGE CURVE

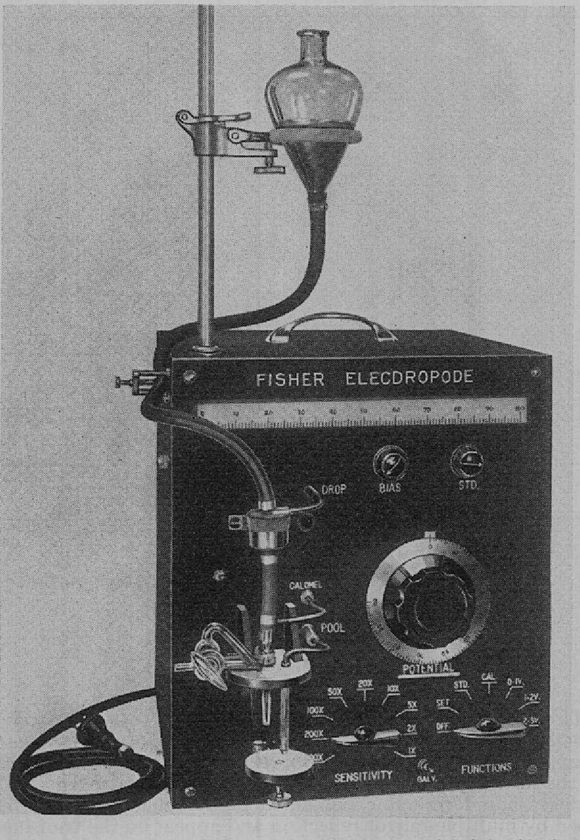
Three potential ranges (0 to 1, 1 to 2, and 2 to 3 volts) may be selected by a switch, and decimal fractions of each range by means of a slide wire. The absolute value of potential is checked in the usual way by balancing potentiometrically against an enclosed standard cell. The galvanometer deflections are magnified by multiple-mirror reflection and appear on the translucent scale at the top of the instrument. Nine ranges of sensitivity are provided by the universal shunt. The polarity of the electrodes can be reversed with a switch which indicates the polarity of the drop. Other controls introduce a bias or compensating current, check the potential of the anode pool, and adjust the mechanical zero of the galvanometer. Considerable merit is to be found in the easily adjusted cell and its provisions for sweeping gas through or over the solution. The curves shown in Figures 165, 166, and 167 were taken with this instrument.

Another example of polarometric analyzer of this class is shown in Figure 170.

In this instrument the setting of the voltage divider is read on a precision voltmeter. Range switches are provided (0 to 1, 1 to 2, and 2 to 3 volts) with coarse and fine adjustment for the working current in the divider circuit and corresponding controls for the applied potential. A sensitive, zero resistance potentiometer-microammeter assembly using a pointer-type galvanometer as a null indicator and the above-mentioned voltmeter are used to measure the current. The sturdy dropping electrode assembly at the left utilizes a large mercury reservoir at the top which utilizes the Mariotte flask principle for constant head and therefore gives a constant dropping rate. This well-constructed instrument is housed in a convenient portable case.

Recording. Heyrovský and Shikata (*127*) invented the polarograph in 1925, for the purpose of relieving the tedium of obtaining current-voltage curves. In principle it consists of a motor-driven voltage divider which is coupled with a recording drum carrying a wide strip of photographic paper. A beam of light is reflected from the galvanometer and focused on the moving paper. The complete current-voltage curve is thus photographically recorded. A complete instrument includes means for standardizing the total voltage impressed across the rotating slide wire, automatic printing of coordinates, and adjustment of the galvanometer sensitivity.

The latest model of the Heyrovský polarograph is shown in Figure 171. The metal housing completely encloses the motor-driven voltage-divider galvanometer and film cartridge. A voltmeter indicates the bridge voltage and a resistor above the meter controls this setting as a vernier to the gross range-setting selector



Courtesy, Fisher Scientific Co.

Figure 168. Manually Operated Instrument for Analysis by Dropping Mercury Electrode

to the right. The galvanometer deflection is conveniently visible to the operator through the translucent scale at the lower right; and at the upper left a similar port carries the applied potential scale. The galvanometer shunt is located at the lower left and the true current values can be calculated by multiplying the indicated shunt ratios by the galvanometer sensitivity (indicated on the deflector scale in microamperes per division). Additional operative conveniences include a switching arrangement whereby the anode can be connected to the center of the bridge wire, which is very useful for waves which begin at zero voltage, and provision for rotating the camera to new positions when several polarograms are to be recorded on a single sheet. A typical application of this instrument is also shown in Figure 171.

The "Electrochemograph" (Figure 172) is a recording polarograph and consists of a polarizing unit which is a precision voltage divider driven by a synchronous motor, an amplifier, and a standard Micromax recording potentiometer. As the manufacturers point out, the amplifier and recorder are standard units which have wide use for many other purposes in the laboratory. The polarizer unit contains a compensated shunt and a capacitor of such magnitude that the time constant of the circuit is equivalent to a galvanometer of 8-second period. The minute currents are amplified before they are passed on to the recorder and for an output of 1×10^{-6} ampere, the sensitivity to current changes is about 2×10^{-9} ampere. The recorder slide wire is calibrated for −40 to 160 millivolts and the scale is divided into 100 uniform divisions marked 20–0–80. Depending upon the current shunt used, each division corresponds, for the minimum range, to −0.2 to +0.8 microampere and for the maximum range to −20 to +80 microamperes.

Since the record is a pen and ink trace, the course of the "electrochemogram" is continuously visible to the operator. The recorder chart is also driven by a synchronous motor and is therefore electrically "locked in" with the polarizer unit. One-half inch space on the chart corresponds to 100 millivolts.

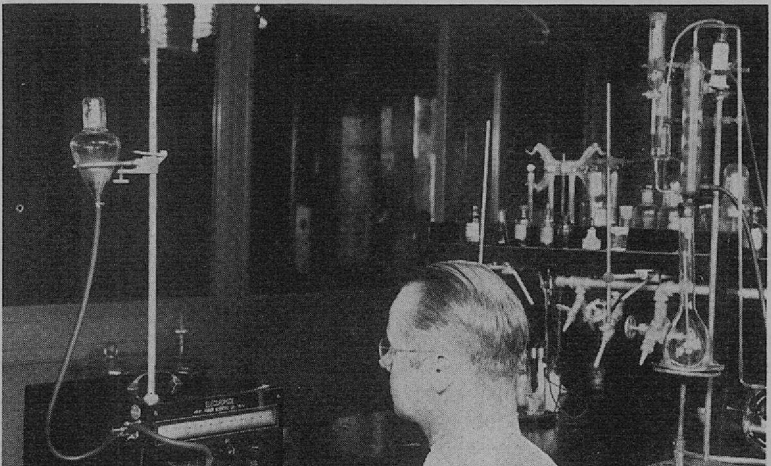
The instrumental approaches to this field have not been exhausted. A few other methods may be mentioned in passing.

The condenser-microammeter method, in which a rugged microammeter replaces the galvanometer and an electrolytic condenser (2000 mfd.) is shunted across its terminals (*161*, page 232). The large condenser practically eliminates oscillations of the needle. For example, with a meter resistance of 4000 ohms, a 2000-mfd. condenser yields an *RC* or time constant of about 8 seconds. Many electrolytic condensers of this class, which are designed for low-voltage filter circuits, may drop to a small fraction of their original capacitance if a potential is not kept across the terminals. In this application no potential of any considerable magnitude is present and this might be expected to occur.

The cathode-ray oscillograph has been applied to the dropping-mercury electrode in three distinct ways, usually not clearly differentiated.

1. By applying a linear voltage sweep synchronized with the drop time (*188*).
2. By applying a small sinusoidal alternating current voltage in series with the direct current potential applied to the dropping electrode. The oscillogram is a sinusoidal wave at a direct current voltage equal to $E_{1/2}$ and is distorted above and below $E_{1/2}$ (*200*).
3. A small sinusoidal alternating current is applied in series with the direct current potential and a phase shift in the region of $E_{1/2}$ is observed on the oscillograph (*24*). In a modification of this scheme, the dropping electrode is connected in a bridge circuit (direct current and series alternating current) and the bridge is balanced for the reactive as well as resistive components. Above and below $E_{1/2}$ the dropping electrode presents a high capacitative reactance. At $E_{1/2}$ the necessary resistance compensation is said to be a measure of the concentration. In the bridge method, no oscillograph is used; instead an amplifier and bridge-balance indicator are used. This is the Dutch equivalent of our "magic eye" (6E5) tube.

Applications. Tables of data are given in several places (*124*, *160*, *161*, *195*, *239*) listing half-wave potentials and tangent potentials of organic substances under various condi-



Courtesy, Fisher Scientific Co.

Figure 169. Use of Elecdropode in a Large Industrial Laboratory

Courtesy, *American Instrument Co.*

Figure 170. Polarometric Analyzer

tions and in different media. Actual procedures for technical analyses are also available (*134*) and will suffice in most cases in deciding whether a given determination is feasible. The Sargent bibliography (*239*) is particularly valuable because full titles of all publications to date (1941) are included.

Amperometric Titrations. A most important extension of general polarographic principles is to be found in the method of amperometric titrations (*161*, page 447, *205*). This field is being developed intensively by Kolthoff and his co-workers. Diffusion currents are measured with the dropping-mercury electrode or microplatinum electrode during the progress of a titration. Several cases are recognized in which the substance or the reagent or both are electroreducible. Accordingly, the diffusion current decreases progressively until the end point is reached, or it is zero until excess reagent appears or a V-shaped curve is obtained. The end point is best obtained graphically as in conductance titrations. Corrections are made for dilution effects. There is a degree of selectivity in this technique not to be found in potentiometric titrations, because the applied potential, which is not changed during the titration, can be selected to correspond with the electroreduction of the desired ion. The advantages and limitations are fully discussed by Kolthoff and Lingane (*161*).

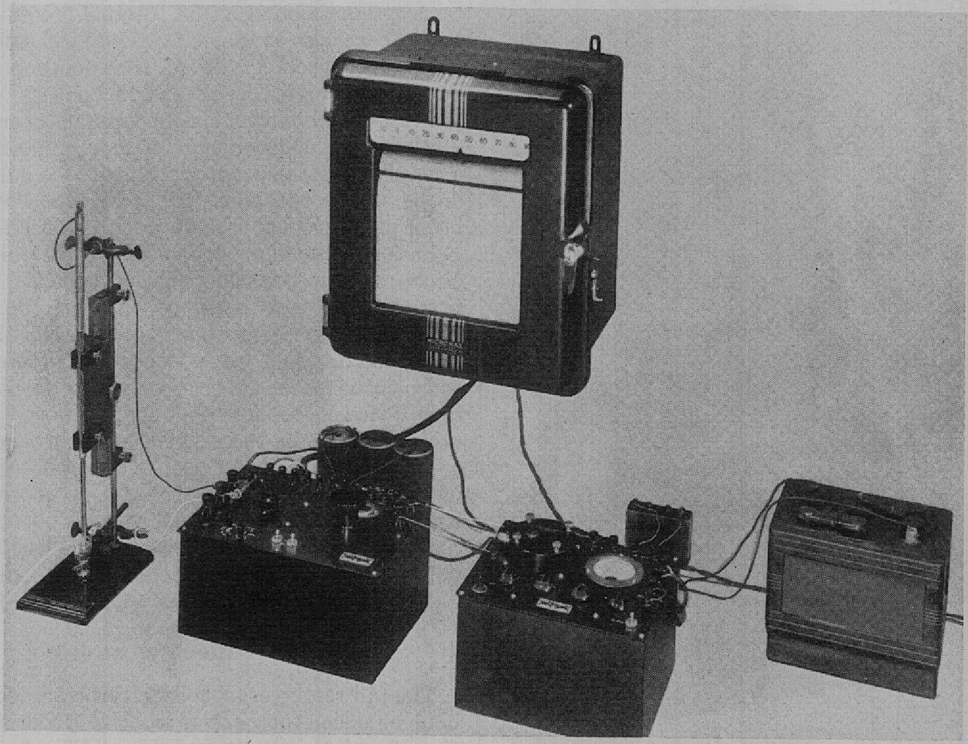
Electrographic

The full resources of Feigl's spot tests (*73*) can be used in unique fashion for cases of analyses which involve the detection of surface impurities and in addition an estimate of their geographic location on the surface. The technique is based on

Courtesy, *E. H. Sargen & Co.*

Figure 171. Heyrovský Polarograph and Use in Determination of Lead in Urine

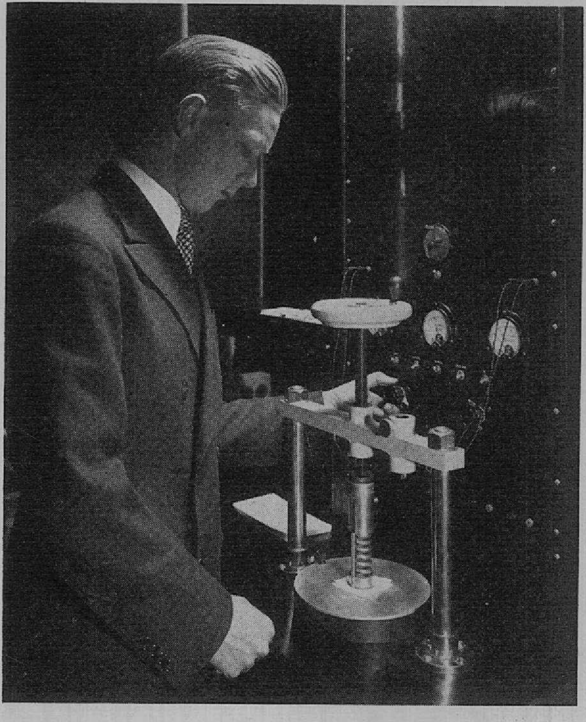
Cells containing prepared specimens are in front row of rack



Courtesy, Leeds & Northrup Co.

FIGURE 172. ELECTROCHEMOGRAPH ASSEMBLY

the early work of Fritz (*82*) and Glazunov (*95*). The technique has been highly developed and improved at the Bell Telephone Laboratories and the following discussion is based largely on the work done there.



Courtesy, Bell Telephone Laboratories

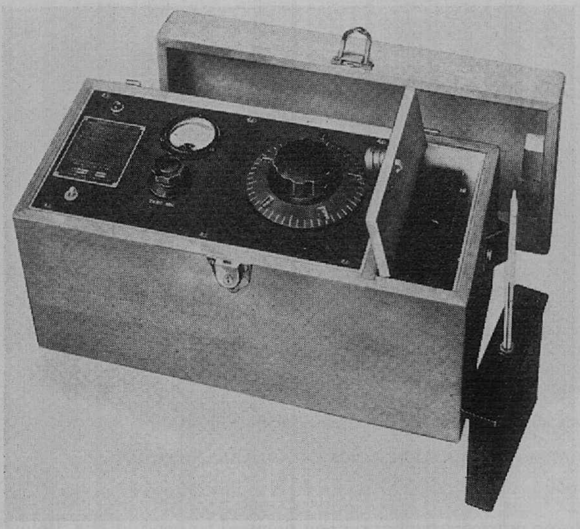
FIGURE 173. APPARATUS FOR ANALYSIS BY ELECTROGRAPHIC METHOD

THEORY. The method depends on the electrolytic deposition of the substances on a reagent-impregnated paper or other suitable matrix. The anode is formed by the test specimen itself and the cathode by some indifferent metal, usually a sheet of aluminum. When a low potential (2 to 6 volts) is impressed, metal ions pass from the specimen into the paper at a rate controlled by the current and in quantity proportional to the time. The deposit produced on the paper may or may not be colored, depending on the choice of reagent, but if it is not it may be suitably "developed" by subsequent treatment of the paper with other reagents. The print is usually sharp because the electric field helps to prevent lateral diffusion. The instrument requirements are fairly simple and the technique is very rapid. The number of available color reactions is very great; indeed, the full resources of Feigl's methods can be utilized.

Very great improvements on some of the original Feigl methods have been made by Clarke and Hermance (*41*)—for example, they have shown that the use of alkali sulfides in test papers is entirely unsatisfactory, since it permits no control of the concentration of that ion. The use of zinc, cadmium, or antimony sulfide provides stable test papers, each of which has its own maximum sulfide-ion concentration and therefore precipitates only those metals whose sulfide solubility products are sufficiently low. The application of these principles to the electrographic technique is an outgrowth of their careful studies and improvements in the spot test technique.

INSTRUMENTS AND APPARATUS. A very convenient arrangement for conducting electrographic tests is shown in Figure 173.

By means of the press illustrated in the foreground an appropriate test paper can be mounted between the specimen and the base plate. The control panel shows meters for measuring the applied potential and the electrolyzing current. Rheostats are provided for adjusting these quantities and an automatic time switch shown above the left-hand meter can be set to control the duration of the "exposure". At an adjacent bench (not shown)



Courtesy, C. J. Tagliabue Co.

FIGURE 174. DIELECTRIC-TYPE MOISTURE METER

complete washing and developing facilities are provided. Small porcelain dishes contain the developing reagents or other media necessary for subsequent development of the image.

Hermance describes this equipment (*119*) as well as completely portable equipment (*120*) for conducting analyses of this type in the field, giving very striking color photographs of technical applications.

APPLICATIONS. A thorough description of the technique has been set forth by Glazunov and Krivohlavy (*96*), who give data for the quantitative determination of nickel in nickel steels and also describe graphic and computational procedures. Jirkovsky (*145*) describes analyses conducted on iron, cobalt, nickel, copper, lead, cadmium, sulfur, bismuth, arsenic, antimony, zinc, and other elements and includes a group of more important references. Hermance's illustrations (*119, 120*) include studies on tinned brass sheet, which provide striking illustration of porous areas and scratches, indicating exactly where the brass has been exposed, and distinctive prints obtained from nickel-palladium duplex metal rod, and of structural elements which have been plated first with nickel and then with chromium.

In the latter case the print was prepared electrographically with the specimen surface in contact with dimethylglyoxime–barium hydroxide paper. When made anodic, the chromium dissolves directly to form yellow barium chromate, while the nickel reacts with the dimethylglyoxime–barium hydroxide to give a red compound. The distribution of the two metals is therefore revealed in a striking red and yellow print and no ordinary black-and-white photograph can do justice to the sharp and convincing nature of the evidence.

Other examples illustrate the detection of traces of copper or of brass on a penknife blade which gave striking proof of suspected vandalism or sabotage. Although spectrographic evidence has been used in similar cases, it is not difficult to decide which bit of evidence would be more convincing to a jury.

The general technique has been extended by Yagoda (*308*) and others to the location of mineral constituents in plant and tissue sections.

An interesting application of this method has been described by Perley (*214*). In seeking the proper location of recording antimony electrode assemblies it was necessary to find one in which copper was present to an extent no greater than 0.1 part per million, since copper ion interferes with the use of the electrode for pH measurements. A rod of pure antimony was immersed in the solution to be tested, after which the replaced copper was electrographically deposited on reagent paper containing sodium nitrate and diethyldithiocarbamate. The latter produces a brown stain if copper is present. Simple portable apparatus was developed, with which an operator can detect 0.1 to 0.5 p. p. m. of the offending ion.

Dielectric Constant

Dielectric constants can be determined with a high degree of precision and the information in the light of Debye's contributions is very useful in elucidating details of molecular constitution. Analytical applications have been few in number (*61, 118*); indeed, empirical industrial uses of this method have been more frequent, and the general technique has been applied to control problems—for example, in making continuous measurements of thickness (rubber sheet, etc.). The high state of development of modern instruments would seem to invite further investigation of its analytical possibilities.

THEORY. The dielectric constant, ϵ, of a medium is given by

$$\epsilon = C/C_0$$

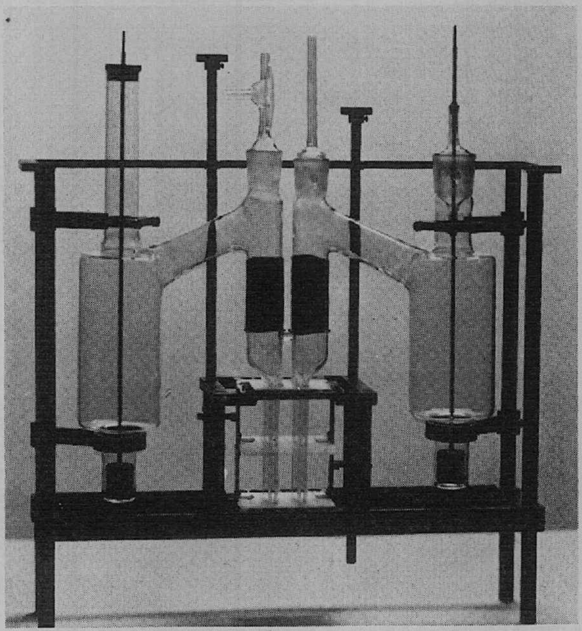
in which C is the capacitance of a condenser with the medium between its plates, and C_0 the capacitance of the condenser with a vacuum between its plates.

For a large number of substances the polarization, P, as defined by the Clausius-Mosotti equation (*44, 193*) is practically independent of the temperature

$$\frac{\epsilon - 1}{\epsilon + 2} \times \frac{M}{d} = P$$

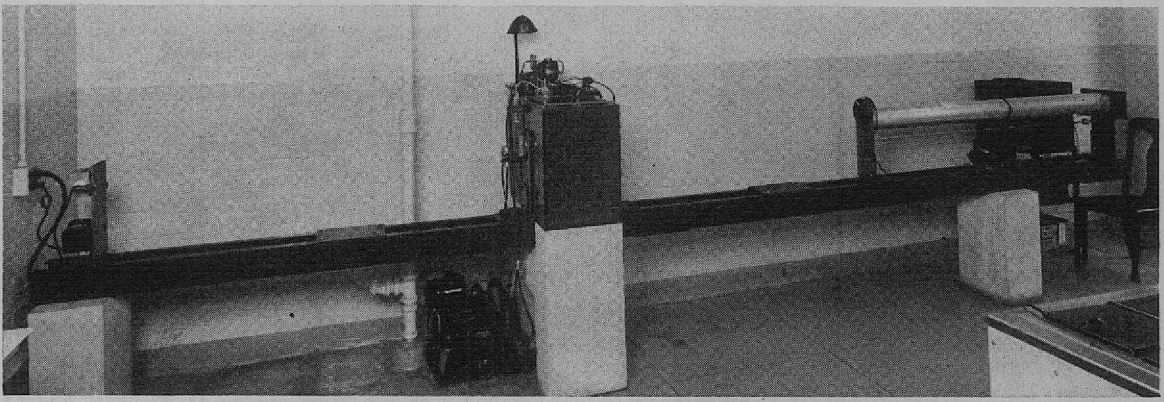
and from the Maxwell relationship $\epsilon = n^2$, where n is the refractive index for long waves, we would expect identity between P and the molar refraction, and indeed the two agree for many substances, provided P is relatively independent of the temperature.

Debye (*52*) has shown that the polarization contains two



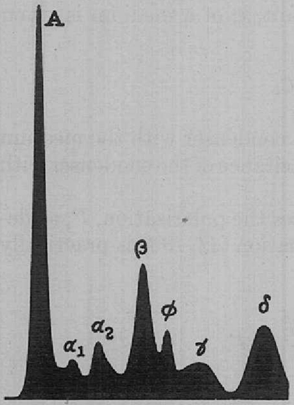
Courtesy, L. G. Longsworth, Rockefeller Institute for Medical Research

FIGURE 175. TISELIUS ELECTROPHORESIS CELL



Courtesy, L. G. Longsworth, Rockefeller Institute for Medical Research

FIGURE 176. COMPLETE APPARATUS FOR ELECTROPHORESIS BY SCHLIEREN SCANNING ARRANGEMENT



Courtesy, L. G. Longsworth, Rockefeller Institute for Medical Research

FIGURE 177. ELECTROPHORETIC PATTERN OF MIXTURE OF PROTEINS IN HUMAN BLOOD PLASMA

contributions, one due to the induced polarization and the other to the permanent dipole moment μ. Thus

$$\frac{\epsilon - 1}{\epsilon + 2} \times \frac{M}{d} = P = \frac{4\pi N}{3}\alpha + \frac{4\pi N}{3} \times \frac{\mu^2}{3kT}$$

It is evident from this expression that the polarization, P, should be a linear function of reciprocal temperature $1/T$ and from the slope of the straight line, one can calculate μ. This equation is the basis for the important contributions which have been made to molecular structure studies.

Courtesy, Burlington Steel Co., Ltd., and Fisher Scientific Co.

FIGURE 178. PLANT USE OF CARBANALYZER FOR DETERMINING CARBON IN STEEL

Some expressions have been derived to predict the dielectric constants of mixtures, involving empirical constants, but in general the dielectric constant reflects all the anomalies of nonideal solutions; indeed, it is one of the most powerful means of investigating deviations from ideal behavior (*261*). This state of affairs does not preclude the use of empirical calibrations for binary or even ternary mixtures, provided the individual ϵ values differ sufficiently. The high value for water (ϵ = 80) makes it possible to measure extremely small amounts of moisture in organic liquids, but by the same token traces of water may complicate the measurement of nonaqueous media.

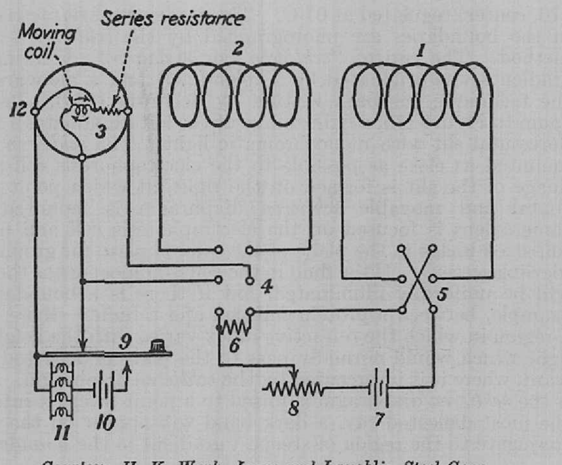
INSTRUMENTS AND METHODS. The dielectric constant is usually measured in terms of the definition which we have given of that quantity—i. e., by measuring the capacitance of a condenser with and without the substance between its plates. Other methods, depending upon resonance, the rate of propagation of electric waves, or a direct measure of the electric force acting through the dielectric are discussed briefly by Smyth (*261*).

Several methods are available for measuring small changes in capacitance. Whatever method is used, it is customary to use the direct substitution, replacement, or compensation technique, in that the measuring condenser is shunted by a high-precision variable condenser. Whatever change occurs in the measuring condenser is cancelled by changing the setting on the precision condenser and since the capacitances of condensers in parallel are additive, the entire burden of precision is placed on the compensator. The rest of the circuit merely indicates when compensation has been effected.

The capacitance bridge is a very convenient instrument for this purpose. Theoretically this consists of a Wheatstone bridge in which the four arms contain pure capacitors and the condition of balance is simple to compute. If a capacitor is "leaky" (finite resistance), the bridge must be balanced for resistance as well as for capacitance, since the currents are out of phase. The balancing of bridges under these conditions has been greatly simplified by oscillograph phase-shift indicators. A very thorough treatment of bridge circuits of all classes is to be found in the monograph by Hague (*103*). The bridge is excited by an oscillator, preferably one with a choice of frequencies. Balance is detected with a crystal detector and galvanometer, or better with one of the electronic indicators (*86*, *87*). Phones can be used if the high-frequency oscillator is slightly modulated at an audible frequency.

In the resonance method an oscillator is used to generate a high frequency. The indicator of this oscillator is coupled to the inductor of the measuring circuit which contains the measuring and compensating condenser. The measuring circuit will have a resonant frequency which is given by

$$P = 1/2\pi\sqrt{LC}$$



Courtesy, H. K. Work, Jones and Laughlin Steel Corp.

Figure 179. Circuit of Carbanalyzer

> If the compensating condenser is adjusted until the frequency of the measuring circuit is equal to that of the generator, the current induced in the measuring circuit will be a maximum. The condition of resonance, for which the current is a maximum, can be measured with a vacuum-thermocouple-galvanometer combination or better by electronic means. The resonance curve—i. e., $I/\omega C$—is quite sharp; the true figure of merit is set by the Q of the circuit, which is the ratio of reactance to resistance. Newer developments in radio engineering have furnished increasingly better "high-Q" circuit components.
>
> The heterodyne or beat-frequency method utilizes two oscillators, one of fixed frequency and the other controlled by the measuring condenser. In each oscillator, the frequency is a function of resistance, inductance, and capacitance. In the reference oscillator these are all held constant; in the measuring circuit, the specimen condenser determines the frequency. If the two oscillators are loosely coupled, a new frequency, which is equal to the difference of the two frequencies, appears and can be isolated with a pick-up coil, amplified, and applied to phones or a loud-speaker. By rebalancing the measuring circuit with the compensating condenser, the heterodyne signal can be reduced to zero frequency (zero beat). In practice, this is beset with some difficulties because the oscillators are likely to "pull in" in a sort of lockstep fashion in the region of zero beat. A still more sensitive method consists in setting not to zero beat but rather to some frequency, such as 1000 cycles, and then "beating" this note against a standard 1000-cycle source.

This general technique is practically identical with dozens of contemporary practices in radio engineering, but few of the refinements of the latter field have found their way into dielectric measurements. Frequency measurements can be made with an extraordinary degree of precision (*197*, Figure 14). Certain extensions of the method are discussed below.

Applications. Very few applications have been made to analytical problems. Schupp (*246*) in investigating pressed powders and various mixed solids, observed difficulties in the pressed-powders technique due to particle size and the applied pressure. Lampe (*167*) also used the method for moisture in sugar, starch, proteins, and fats and since $\epsilon < 10$ for most of these substances compared with the value for water ($\epsilon = 80$), the value is sensitive to traces of moisture. A recent successful application is illustrated in Figure 174, the dielectric-type moisture meter. The widespread use of this company's conductance-type moisture meter (Figure 160) in official and industrial laboratories has provided ample experience in the demands made upon a practical moisture meter.

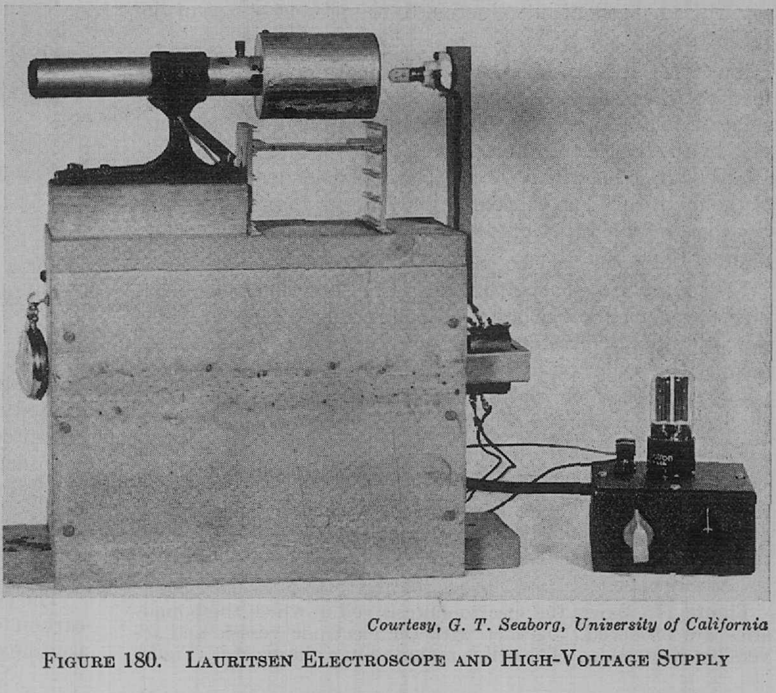
> It is intended for use with granular materials such as grains, cereals, and other powdered substances. It is a self-contained alternating current line-operated instrument which uses the heterodyne beat principle. The master oscillator is crystal-controlled and beats against the measuring oscillator, the frequency of which is controlled by the measuring condenser and its parallel compensating condenser. The two frequencies are mixed in part of the master oscillator tube (a pentagrid converter tube), a practice which is common to superheterodyne broadcast receivers. This practice minimizes the tendency of the oscillators to "pull in" and maintains a relatively loose coupling between the two. The difference or beat frequency is rectified by a diode element in one of the tubes and is then fed to a microammeter, which is shunted with a resistor-condenser network to provide a suitable time constant. The measurement consists in adjusting the compensating condenser until the meter reads zero. Small oscillations of the needle will result as this setting is approached, and at the exact setting the motion ceases. Maximum deflections occur at a beat frequency of ca. 200 cycles per second on either side of the true zero setting. The sample condenser consists of two parallel metal plates between which the substance is packed. A satisfactory technique has been worked out for doing this in a sufficiently reproducible manner.

Dielectric measurements are worthy of further study from the analytical viewpoint. The electrical developments are far beyond the chemist's most exacting requirements. There is no scarcity of data, but most of them would have to be recalculated to an analytically useful basis, because the emphasis for the most part has been on questions of theoretical interest, relating to dipole moments and changes in polarization in mixtures as a function of composition.

In addition to the sources mentioned above, reference to treatises on electronics and radio engineering (*222*, *272*) is essential for an appraisal of contemporary practice.

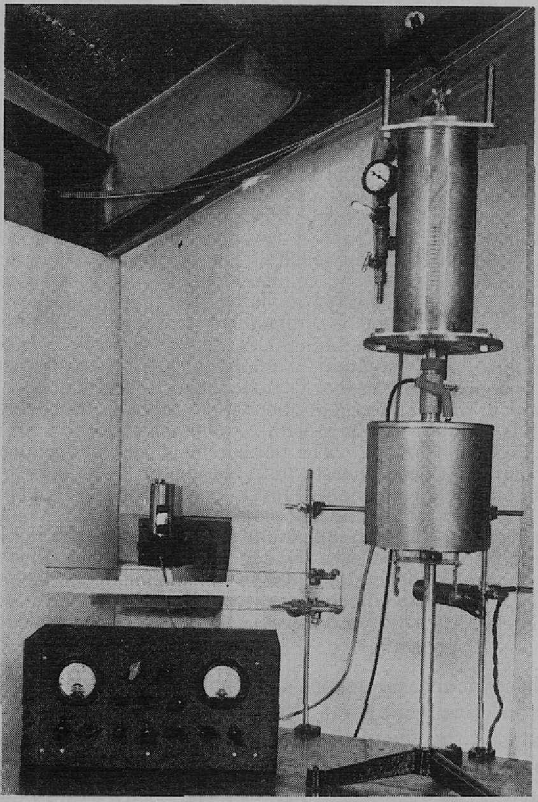
Electrophoretic

Since the phenomenon of electro-osmosis was discovered by Reuss in 1808, the vast field of electrokinetic phenomena has developed. Of the many phenomena and important principles



Courtesy, G. T. Seaborg, University of California

Figure 180. Lauritsen Electroscope and High-Voltage Supply



Courtesy, G. T. Seaborg, University of California

FIGURE 181. IONIZATION CHAMBER AND ELECTROMETER MEASURING CIRCUIT

included in this field (*2*), none is more timely and significant than the study of proteins by the electrophoretic effect. That such studies have succeeded in providing accurate means for analyzing these complex substances is a triumph of first order, comparable only to the alternative and complementary technique of the ultracentrifuge. This interesting and important field was the subject of a recent symposium (*3*) in which some of the leading American investigators participated, and should serve as an excellent introduction to the present status of the subject.

THEORY. In the moving boundary method for analyzing a mixture of proteins, the initially sharp boundary between a solution of the proteins and the buffer solvent will, on passage of an electric current, separate into a number of boundaries, each moving with a velocity characteristic of a component of the mixture. The concentration changes so produced give rise to refractive index gradients, which can be measured in a number of ways.

METHODS AND INSTRUMENTS. Investigations providing precise means for the study of electrophoretic boundaries were initiated by Tiselius (*274, 275*). At present the methods include the scale method due to Lamm (*166*), the diagonal *schlieren* method of Philpot (*216*) and Svensson (*271*) and the *schlieren* scanning method of Longsworth (*176–178*). The light-absorption method (*3*) is restricted to colored substances or the use of ultraviolet light with prohibitively expensive quartz optics. Since the *schlieren* scanning method yields analytical results with less computational labor than the others, it will be described and illustrated briefly.

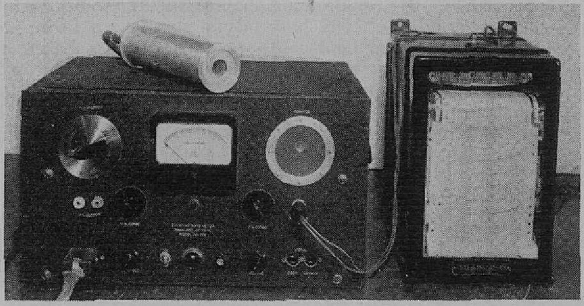
Figure 175 shows the electrophoresis cell in which the boundaries are observed, together with the electrode vessels and reversible electrodes. The cell is mounted in a thermostat (Figure 176, center) regulated at 0° C. The gradients of refractive index in the boundaries are photographed by the *schlieren* scanning method. The use of "*schlieren*" or striae for observing such gradients was originated by Töpler (*276*) and a monograph on the technique has been written by Schardin (*240*). Referring again to Figure 176, a light source at the left illuminates a narrow horizontal slit with monochromatic light. The *schlieren* lens is mounted as close as possible to the electrophoresis cell and an image of the slit is formed on the right, at which point a horizontal and movable *schlieren* diaphragm is mounted. The camera lens is focused on the electrophoresis cell and forms a full-sized image in the plane of the camera plate (or ground-glass viewing screen). If the fluid in the cell is homogeneous the image will be uniformly illuminated, but if there is a boundary—for example, between a protein solution and a buffer—there will be a region in which the refractive index varies with the height, and light which would normally pass to the plate is deflected downward, where it is intercepted by the *schlieren* diaphragm. Hence if the *schlieren* diaphragm is raised to a point where it intercepts the most deflected ray, a dark band will appear on the screen, conjugate to the region of steepest gradient in the boundary.

The great advance made by the Longsworth improvement consists in the use of a narrow vertical slit in the plane of the plate and in imparting to the camera plate a uniform horizontal motion. The motion of the plate is coordinated by interchangeable gears with the vertical motion of the *schlieren* diaphragm.

APPLICATIONS. A representative result is shown in Figure 177, which is a photograph of the electrophoretic pattern of a typical mixture of proteins—namely, human blood plasma.

Each peak in the pattern, except that marked δ, corresponds to a component of plasma—namely, *A* albumin, α_1, α_2, β, and γ globulins, and ϕ fibrinogen. The concentration of each component is proportional to the area under the corresponding peak.

The precision of the method is limited only by diffraction phenomena and at present corresponds to about 0.00002 in refractive index—i. e., 0.01 per cent in protein concentration.



Courtesy, R. D. Evans, Massachusetts Institute of Technology

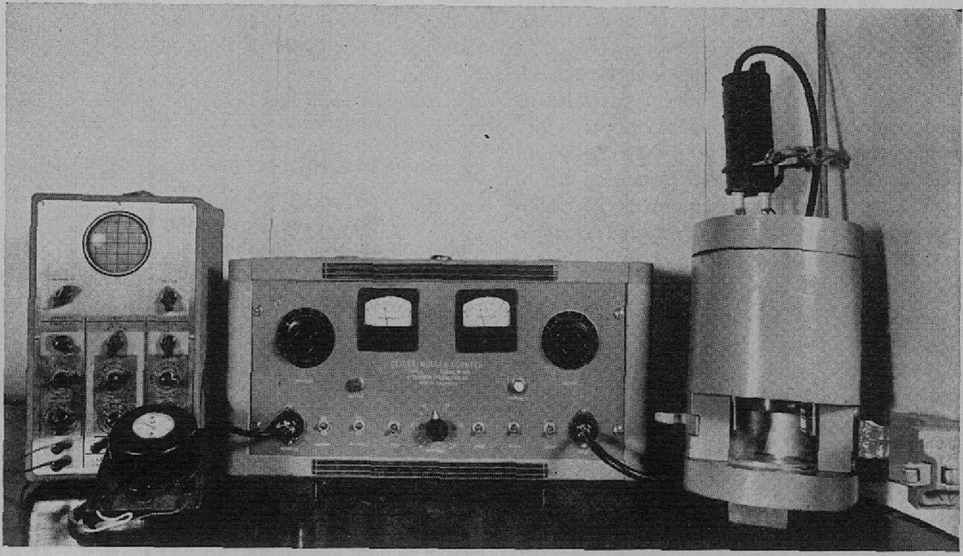
FIGURE 182. GEIGER-MÜLLER COUNTER APPARATUS WITH BELL-TYPE BETA-RAY COUNTER

For a more extensive list of applications the reader is referred particularly to Longsworth (*179*).

Magnetic

The analytical applications of magnetic properties are very limited and few in number. Almost without exception, the measurements are limited to the use of the Gouy balance in conjunction with a powerful magnet. The magnetic susceptibility is a general unspecific property measurable for all states of aggregation and is difficult to measure if high precision is required. It is not surprising, therefore, that practical uses are largely confined to ferromagnetic materials.

The successful correlation between these properties and the carbon content of steels has been mentioned (*197*). The routine examination of a test specimen is shown in Figure 178



Courtesy, G. T. Seaborg, University of California

FIGURE 183. GEIGER-MÜLLER COUNTER ASSEMBLY

and the circuit for the analyzer is shown in Figure 179. The circuit and the general development of this method have been described by Work (*303*).

Radiometric

THEORY. A single radioelement is characteristically defined and identified by its rate of decay, which is given by

$$-dN/dt = \lambda N \qquad (14)$$

or the number of atoms remaining after time t is

$$N_t = N_0 e^{-\lambda t} \qquad (15)$$

where λ = disintegration constant. Another convenient designation is the half-life, T, which is the value of t for which

$$N_t = \frac{N_0}{2}$$

and from which

$$T = \ln 2/\lambda = 0.69/\lambda \qquad (16)$$

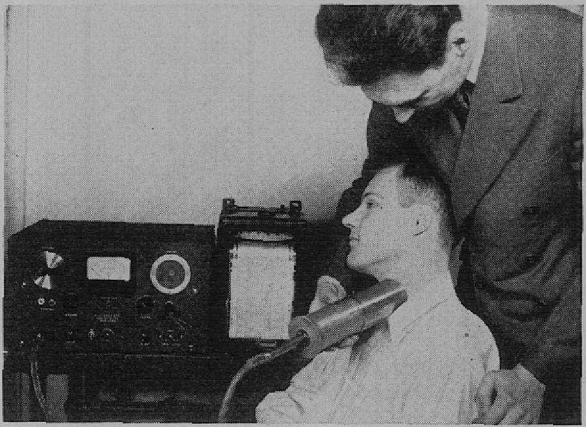
If the product of disintegration itself disintegrates, the same type of expression holds and the total activity of the system can be expressed by a simple mathematical extension of the above principle. The various cases for successive transformations are discussed by Rutherford (*235*).

The particles or radiation emitted during disintegration may be detected photographically, by excitation of a fluorescent screen (spinthariscope), or by ionization produced in a gas. In the latter case the process may be rendered visible (C. T. R. Wilson cloud chamber) or measured by appropriate electrical methods.

The unit of intensity in radioactivity is the curie. A curie of any radioactive material undergoes the same number of disintegrations per unit time as 1 gram of radium—i. e., 3.7 × 10^{10} disintegrations per second (*247*). The type of radiation is classified as follows (*247*):

e^- = negative beta particles
e^+ = positive beta particles (positrons)
γ = gamma rays
e = internal-conversion electrons
K = K-electron capture
$I. T.$ = isomeric transition (transition from upper to lower isomeric state).

Positron emission is always accompanied by "annihilation" gamma radiation, since each positron with an accompanying electron is annihilated and this destruction of mass results in 2 gamma rays each having an energy given by mc^2—i. e., 0.51 Mev. (million electron volts). The previously mentioned methods of detection must be supplemented by further refinements in order to establish with certainty the type or mechanism of disintegration—for example, closed tracks are usually examined in a magnetic field and coincidence counters are used to determine the energy of gamma rays.



Courtesy, R. D. Evans, Massachusetts Institute of Technology

FIGURE 184. USE OF COUNTING RATE METER FOR DETERMINATION OF RADIOACTIVE IODINE IN THYROID OF A PATIENT

ARTIFICIAL RADIOACTIVITY. Before the discovery of artificial radioactivity by Irene Curie and Frédéric Joliot in 1934, analytical applications were limited to the relatively few naturally occurring radioactive isotopes, and although several ingenious schemes were developed to make indirect use of them, the field showed relatively little promise of extensive use. This earlier work is treated by Hahn (*105*) and by Ehrenberg (*66, 67, 210, 211*). Recent tables (*174, 247* (list more than 350 artificial radioactivities, and radioactive isotopes of 87 elements have been produced (see also *123*, *217*).

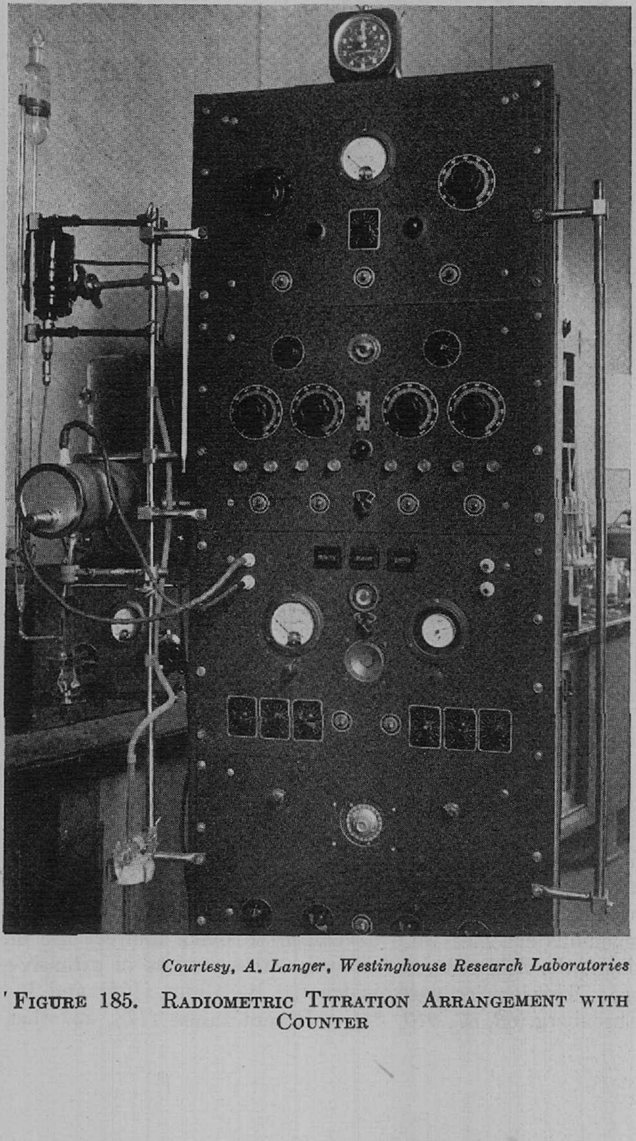
They are prepared by bombarding a suitable target by neutrons (n), protons (p), deuterons (d), alpha particles or helium nuclei (α), electrons (e), and gamma rays (γ). Only the first four projectiles are important for preparing useful amounts of the isotopes. The bombardment is carried out in one of the various types of high-voltage apparatus, of which the magnetic resonance accelerator or cyclotron of Lawrence (*116*, *171*) is an outstanding example. Neutron sources using naturally occurring radioactive substances may also be used, but the yields are smaller (*5*). In this type of source, the α particles emitted by radium, radon, or polarium bombard beryllium, which then emits neutrons. Their range or energy may be modified by screens of paraffin or other substances rich in hydrogen atoms.

The production of a radioelement may be represented by an equation such as the following:

$$_{11}Na^{23} + {_1D^2} \longrightarrow {_{11}Na^{24}} + {_1H^1} \qquad (17)$$

for the formation of radiosodium by bombarding ordinary sodium with high-speed deuterons, the other product being a proton where the subscript indicates the atomic number and the superscript the mass number of the isotope. The newer and more convenient description is to designate the projectile and the emitted particle; thus the above is a (d, p) reaction. Of the four useful methods, the following types of reactions have been observed and are listed more or less in the order of their probability:

Neutron reactions (n, γ), (n, p), $(n, 2n)$, (n, α), (n, n)
Proton reactions (p, n), (p, γ), (p, α), (p, p)
Deuteron reactions (d, p), (d, n), (d, α), $(d\text{-}2n)$
Alpha particle reactions (α, n), (α, p), (α, d), $(\alpha, 2n)$, (α, α)



Courtesy, A. Langer, Westinghouse Research Laboratories

FIGURE 185. RADIOMETRIC TITRATION ARRANGEMENT WITH COUNTER

This terminology designates the process; the complete statement also specifies the target, so that Equation 17 is abbreviated to Na-d-p. Thus the four methods for preparing radiosodium may be abbreviated as Na-n-γ, Mg-n-p, Al-n-α, Mg-d-α. In the last case, the effective target is really the stable isotope of magnesium (Mg^{26}), which is present to the extent of 11.1 per cent in ordinary magnesium.

The valuable table by Seaborg (*247*) gives complete information on more than 350 artificial radioelements, listing the atomic number, mass number, degree of certainty of the assignment, type of radiation emitted, half life, energy of the radiation (particle and gamma rays) in Mev., and the various modes of production. Another table in this splendid paper lists the stable isotopes of the elements, giving mass numbers and the relative abundance of the various isotopes. These tables really provide a list of "reagents" for the prospective investigator and he can form in advance a fairly good opinion of their suitablity for a given problem.

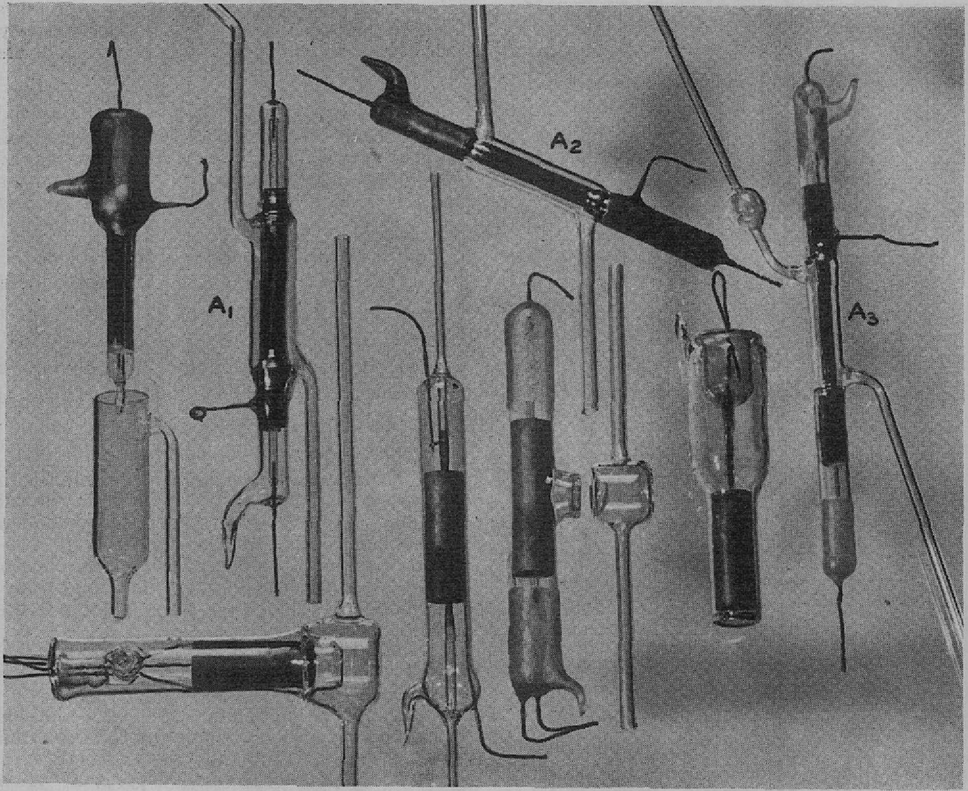
SEPARATION OF RADIOELEMENTS. The preparation of a radioelement is one thing; its isolation or concentration in a form suitable for use is another and requires considerable care and ingenuity. The various methods have been reviewed and classified (*227*, *247*). The techniques may be grouped as follows (*227*):

1. Electrochemical
    Gas phase
    Liquid phase
2. Chemical
3. Extraction
    By solvents
    By absorbents

If the radioelement which has been formed is not an isotope of the target element, its removal is facilitated by the addition of a small amount of the corresponding inactive isotope ("carrier") and it is then subjected to the usual methods of chemical separation. In general, it is desirable to maintain a high "specific activity"—that is, ratio of active to inactive isotope. There is still ample opportunity to discover new chemical procedures to improve and refine this part of the problem (*76*).

It may be of interest to appraise the "production facilities" of modern devices. Under the best conditions, amounts of the radioelements can be prepared which are just about weighable. Thus, according to Seaborg (*247*), a 4-hour bombardment of phosphorus with 100 microamperes of 16-Mev. deuterons produced about 50 millicuries of P^{32}. From the known disintegration constant this can be shown to correspond to about one-sixth microgram of radioactive P^{32}. Another aspect of the situation may be inferred from the statement of Kurie (*163*) that the demands put on the 37 inch cyclotron at Berkeley are so great that it is operated about 19 hours a day. This places such a great premium on efficient bombardment that the maximum current is employed and pure elements instead of compounds are used. The fact that nearly a kilowatt of energy must be dissipated in the target indicates the enormous energies involved, not to mention many technical and operative difficulties encountered in maintaining an intact target.

MEASUREMENT OF RADIATIONS. The choice of detector is governed by the type of radiation which is to be measured as



Courtesy, A. Langer, Westinghouse Research Laboratories

Figure 186. Types of Liquid Counters

A_1, A_2, A_3. Liquid-jacket-pipet counters used for titration

well as the sensitivity and stability which are required. In general, the measurement is based on determination of the ionization produced by the radiations.

One of the simplest devices is the Lauritsen quartz-fiber electroscope (*170*). The instrument is somewhat similar to a gold-leaf electroscope, but it is much reduced in size and uses a gold-coated quartz fiber in place of a gold leaf. The deflection of the fiber is measured with a low-power microscope provided with a micrometer ocular. The response is linear over 0.6 to 0.7 of the scale range, or over the entire range by offsetting the zero point. With a 3μ quartz fiber the average sensitivity is about 1 division per volt. The capacity of the unit is about 0.2 cm.; therefore, the ion sensitivity is about 1.5 million ions per division. Slightly higher sensitivities may be obtained (700,000 ions per division) by using a lighter fiber. In terms of radioactivity measurements, this instrument works best for intensities of the order of microcuries (10^{-6} curie), although 10^{-7} or 10^{-8} curie can be measured under the best conditions (*247*).

The sensitive element may be placed right in the ionization chamber; indeed, it can be placed in a volume as small as 0.5 cc. and used in thimble chamber measurements.

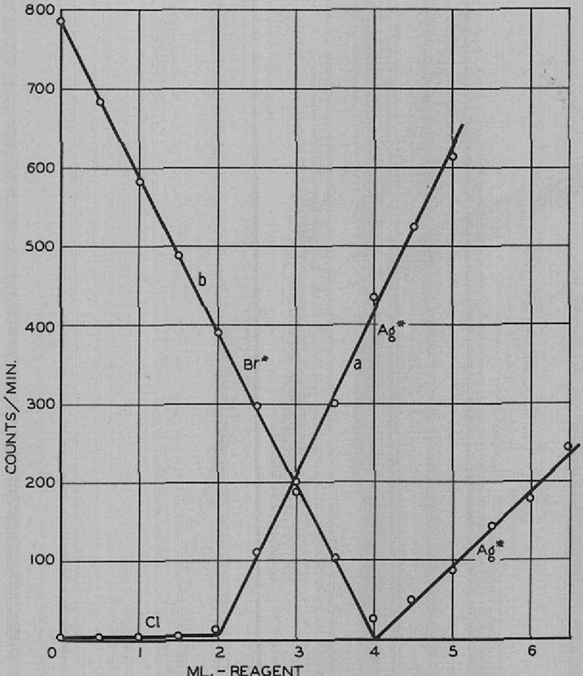
Many investigators view with suspicion instruments of such high sensitivity and suspect instability and temperamental behavior. It is encouraging to note that in connection with cosmic ray measurements a torsion type of fiber electroscope has been developed (*269*), with almost complete freedom from orientation effects, which could be mounted within 3 feet of the engine of a pursuit plane.

A typical installation is shown in Figure 180 in which the Lauritsen electroscope is mounted in an ionization chamber. An adjustable sample tray is mounted under the chamber, and a small lamp, operated from a filament transformer, is used to illuminate the fiber. A small power supply at the right supplies the direct current high voltage for charging the electroscope.

Electrometer and Ionization Chamber. A somewhat more sensitive arrangement of the integrating type is obtained with an ionization chamber to which an electrometer is connected.

The ionization chamber consists of an outer metal cylinder fitted with a well-insulated central, coaxial electrode. A high direct current potential (300 to 400 volts) is maintained across the pair. The potential is high enough to collect the ions before they can recombine (saturation current). Any gas may be used in the chamber; if very penetrating radiation is to be measured, the pressure of the gas may be increased. The ionization current is measured with a sensitive electrometer. Although any sensitive electrometer may be used, such as the Edelmann or Perucca, the present trend is in the direction of stabilized vacuum tube electrometers. In these arrangements, the ionization current is measured by a single-tube direct current amplifier.

Several papers have been published (*58, 263, 279, 287*) dealing with the theory, construction, and operation of these circuits. Equations have been derived indicating the correct values for circuit constants in order to eliminate or minimize changes in the tube constants and fluctuations in supply voltages. In general, special "electrometer" tubes, such as the General Electric FP54, Western Electric D-96475, R. C. A. A-154, or Westinghouse DR+1-506 or 507, are used. These are specially constructed for the difficult problem of measuring very feeble currents from high-resistance sources (*196*). It is likely that the modern inverse-feedback amplifier, with its extraordinarily high stability, will soon replace the galvanometers which are at present used in tube electrometer circuits. However, the electrometer tube itself will still



Courtesy, A. Langer, Westinghouse Research Laboratories

FIGURE 187. RADIOMETRIC TITRATION CURVES

a. Chloride with radioactive silver nitrate
b. Bromide (with radioactive bromine) with radioactive silver nitrate

be used in the first stage, primarily for its transfer characteristics.

The combination of ionization chamber and electrometer is capable of measuring very weak samples. Tube electrometers can attain sensitivities of the order of 10,000 divisions per volt or charge sensitivities of the order of 5×10^{14} divisions per coulomb (*269*). This corresponds to radioactivities of about 10^{-4} microcurie (*247*).

Figure 181 illustrates a typical installation of an ionization chamber. The cylindrical brass container above the ionization chamber, with provision for evacuation and desiccation, contains the vacuum tube and part of the vacuum tube electrometer circuit. The remainder of the vacuum tube electrometer circuit is contained in the cabinet, above and behind which are located the galvanometer and scale.

GEIGER COUNTERS. The Geiger counter is sensitive to individual ionizing particles and depends for its high sensitivity upon ion-magnification. The ions produced by the primary particle are moving in an intense electric field and, by collision, produce thousands of other ions.

Three general classes of counters are recognized.

The Point Counter of Geiger (*88, 236*) consists of a pointed wire placed axially within and insulated from a metal cylinder. A high potential of 1500 to 5000 volts is applied across the electrodes through a high resistance of the order of 10^9 ohms. The point is negative with respect to the cylinder. When an ionizing particle enters the counter a discharge takes place which continues until the potential drops below that necessary to maintain the discharge and the system returns to the normal sensitive state, ready for another count. The change in potential across the series resistor may be detected by a string electrometer or a pulse amplifier. The magnitude of the pulse is more or less independent of the number of ions originally produced by the ionizing particle.

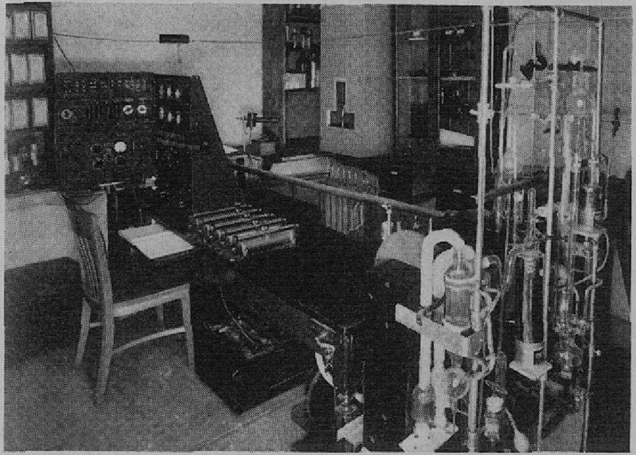
The Proportional Counter of Geiger and Klemperer (*89*) contains a small ball or sphere at the end of the wire, and in this case the wire is made positive with respect to the cylinder. With this arrangement the pulse is approximately proportional to the original ionization produced by the particle and one can distinguish between heavy particles, such as α particles, protons, and deuterons, and lighter particles such as electrons. A linear amplifier is used to measure the pulses.

The Zählrohr or Geiger-Müller Counter (*90*) provides a large area sensitive to ionizing particles. It consists of a cylinder and a coaxial wire between which a high potential is applied. The counter is filled with a suitable gas at reduced pressure. The bursts are detected with an alternating current pulse amplifier and can be made to operate mechanical counters.

Geiger counters have been the subject of many investigations and scores of applications. An excellent treatment from a very practical viewpoint is given by Neher (*204, 269*). Because of their extensive use in cosmic ray research as well as in radioactivity, a large number of special circuits have been developed for accomplishing special tasks. A few of these may be mentioned.

1. For extremely fast counting, where the inertia of mechanical message-counters sets an upper limit, extensions of the Wynn-Williams (*307*) scale-of-two circuit may be employed. Here the actual count is divided exactly in half; two tubes count the bursts alternately. The adding of more scale-of-two circuits may be continued indefinitely, the final tube with its recorder reading 2^{-n} of the original pulse where n is the number of such circuits.
2. Special circuits have been developed to help the Geiger-Müller counter extinguish itself and thus increase the efficiency at high counting rates (*204, 269*).
3. Coincidence-circuits have been developed (*228*) which record a count only if two or more G-M counters have discharged simultaneously. Since all counters register a minimal "background" count due to cosmic rays and radioactive contamination, an appropriate arrangement of coincidence-counters can be utilized to rule out or minimize these accidental registries.'
4. Counting-rate meters have been developed (*72, 94*) which will take randomly distributed pulses of any voltage, shape, and varying magnitude, convert them into uniform pulses (amplitude and duration) and feed them into an amplifier having a capacity-resistance tank circuit which performs a smoothing or averaging process. The output meter thus records the average rate of counting. Rates between 30 and several thousand counts per minute can be accommodated. The output can also be recorded with a recording galvanometer or milliammeter. An illustration of this type of instrument is shown in Figure 182. Preliminary details of its design and operation have been published (*151*) and a complete description will appear soon. A special bell-type beta-ray counter (*245*) with a pre-amplifier mounted in the cylindrical housing is shown resting on the top of the main amplifier cabinet. The pen recorder on the right provides a continuous ink record of the counting rate *vs.* time.

Another installation is shown in Figure 183. The lead shield on the right contains the Geiger-Müller counter tube. The unit



Courtesy, T. I. Taylor, University of Minnesota

FIGURE 188. MASS SPECTROGRAPH

in the center houses the vacuum tube high-voltage supply, amplifier, and scaling unit. In the left foreground is a Cenco impulse counter and behind it is a cathode ray oscillograph for monitoring purposes.

Applications. Atoms or the molecules containing them may be "tagged" with a small amount of their radioactive isotope and their subsequent behavior in any analytical scheme can be followed by measurements with one of the instruments described above. This presupposes the availability of a sufficiently long-lived isotope and a preparation of reasonably high initial intensity. A biological application of tagged atoms is illustrated in Figure 184, in which the counting-rate meter is used for a quantitative determination of the amount of radioactive iodine accumulated in the thyroid of a patient. In ordinary analytical separations, the method may be used to determine completeness of precipitation, coprecipitation, or distribution between solvents. Specific examples of these and many others are discussed in recent reviews (*76*, *121*, *247*).

Another method which has great possibilities for the detection of minute amounts of impurities is to subject the material to bombardment and produce the radioactive isotopes of the impurity. By this means 6 parts per million of gallium in iron have been detected, small amounts of copper in nickel, and of iron in cobalt, etc. Again, one part of copper in 10,000 parts of silver has been detected by bombarding the silver with α particles (*150*).

An interesting combination of techniques has been described by Langer (*169*). Radioactive phosphorus P^{32} was converted to a soluble phosphate, several drops of which were added to a disodium phosphate solution. This was then used to perform several representative titrations (Ba^{++}, Pb^{++}, Th^{++++}, Mg^{++}, UO_2^{++}). After each addition of the reagent, the filtered solution was sucked up into a special chamber surrounding a Geiger-Müller counter. A counting-rate meter (*94*) was used to measure the activity. The end points could be determined accurately, by the intersection of the activity curves.

Figure 185 shows the apparatus used for these measurements, and Figure 186 some examples of liquid counters suitable for analytical work. Through the courtesy of Dr. Langer, the unpublished results of some further work are shown in Figure 187.

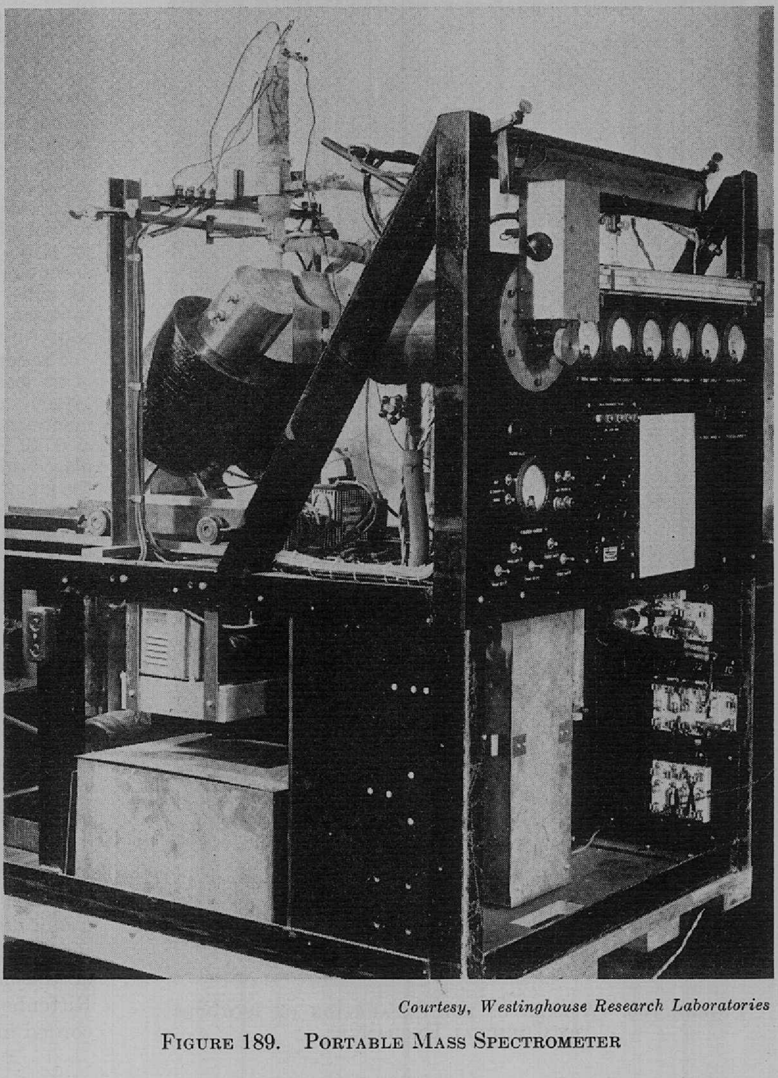
Conclusion. It is difficult to appraise the significance of this mode of analysis; although the field of artificial radioactivity is but seven years old, nearly six hundred papers have been published. The main interest lies in the nuclear studies, and the analytical applications have been relatively few but nevertheless very important and revolutionary. For some time to come, the radioactive isotopes as "reagents" will continue to be scarce, for their preparation is very costly. On the other hand, there are few fields of investigation so well provided with refined and sensitive instruments. Nuclear physics and chemistry have attracted the most brilliant and gifted investigators and ample support for their work has been freely given. Such is the tempo that any textbook on the subject is likely to be out of date before it leaves the press.

Mass Spectrographic

The mass spectrometer or spectrograph is a device in which gases or vapors can be subjected to bombardment by electrons of controlled velocity. The molecular fragments which are ionized can be sorted out by combined electric and magnetic fields and brought to a focus on a photographic plate or on an exit slit. In the case of the spectrograph the ion beam is brought to a focus in the plane of the photographic plate and the resulting mass spectrogram contains lines, the spacing of which depends upon the e/m values of the respective ionic species.

In the mass spectrometer the electric or magnetic focusing fields are so adjusted as to bring one species after another to a fine exit slit, behind which there is placed a Faraday cage which collects the ions. This positive ion current is a measure of the abundance of the particular ionic species that has reached it. By either of the methods it is possible to sort out the molecular ion fragments according to their relative masses and abundance.

This very valuable technique is based on almost half a century of fundamental work by J. J. Thompson, F. W. Aston, Dempster, Smyth, Hogness and Lunn, Bleakney, and others. Among the many contributions to physical science which this technique has made may be mentioned the determination of the relative abundance of naturally occurring isotopes, from which "mass defects" can be computed.



Courtesy, Westinghouse Research Laboratories

Figure 189. Portable Mass Spectrometer

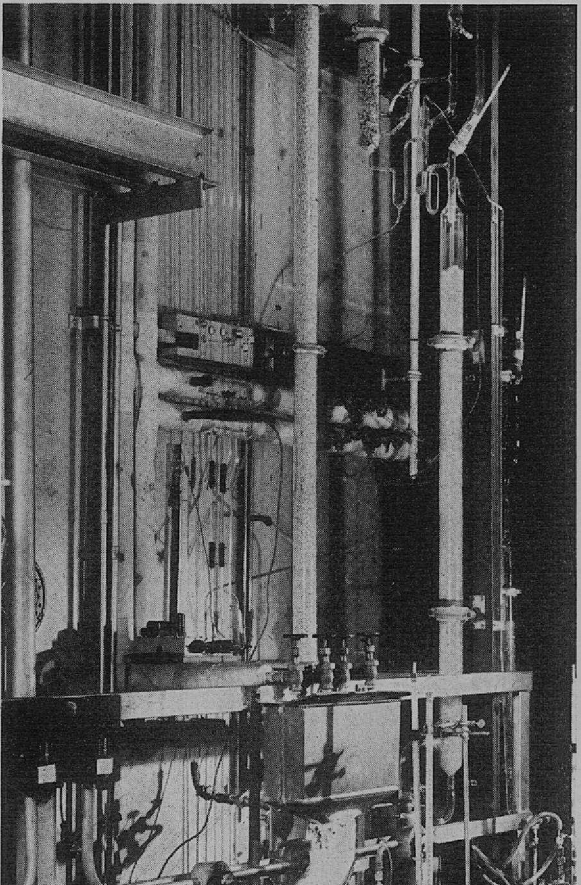
From the analytical view point its value resides in the following possibilities:

1. In the use of stable isotopes for tracer work, it is the most accurate and reliable means of analysis.
2. It is able to determine small traces of certain gases in mixtures with a high degree of certainty and identification.
3. It is adaptable to very small amounts of material, since the total gas pressure maintained in the spectrometer is of the order of 10^{-4} mm. of mercury.
4. Continuous changes in composition can be followed.

In general, the sample must be in the form of a gas or a vapor and although it is possible to work with any of the metals in the vapor form, this, as might be imagined, is beset with certain technical and manipulative difficulties. In some cases, such as the alkali metals, salts can be heated, resulting in the thermionic emission of the metals as positive ions, which can then be resolved by the electric and magnetic fields of the spectrometer.

INSTRUMENTS. Two handsome examples of the mass spectrometer may be discussed briefly.

In Figure 188 is shown the mass spectrometer used by Taylor at the University of Minnesota. It is a Dempster 180° focusing type, designed to measure the abundance ratio of isotopes. It is similar in construction to those described by Bainbridge (*10*) and Brewer (*28*). The analyzing chamber between the poles of the magnet is equipped with an interchangeable ground-glass joint to facilitate the use of different positive ion sources. A small platinum disk impregnated with an alkali element and heated with a tungsten filament serves as a source of positive ions for these elements. Gaseous substances can be admitted to the system through a fine capillary tube, after which they are ionized by bombardment with a beam of electrons. The ions are accelerated into the magnetic field by use of a high-voltage rectifier unit. The resolved positive ion current is measured with a F. P. 54 tube electrometer circuit of the DuBridge and Brown type (*58*).



Courtesy, Eastman Kodak Co.

FIGURE 190. APPARATUS FOR SEPARATION OF ISOTOPES BY CHEMICAL EXCHANGE

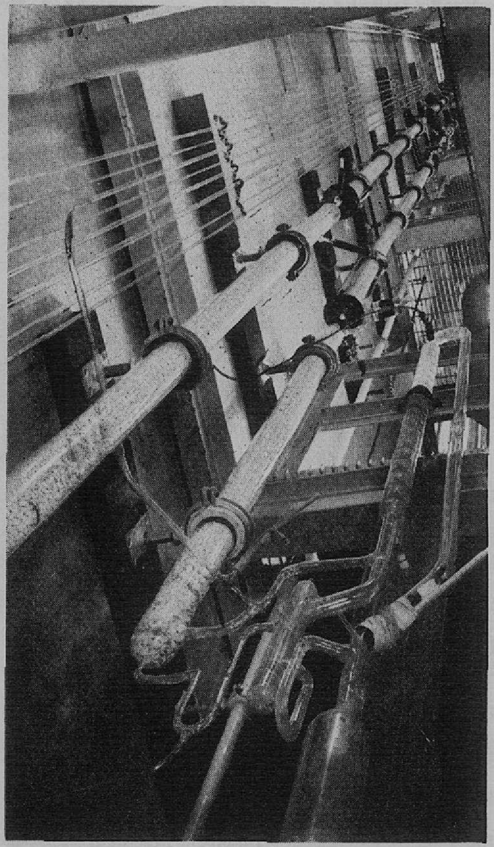
The spectrometer unit with its associated magnet and high-vacuum pumps appears on the right. The electrometer unit and control panels are at the extreme left, sufficiently removed from the local field of the magnet and connected with the Faraday cage of the spectrometer by the long horizontal tube which is carefully shielded and grounded.

The portable mass spectrometer shown in Figure 189, which was designed and built at the Westinghouse Research Laboratories by John A. Hipple, Jr., embodies all the latest improvements in this field. A tentative description (August 1, 1941) has been prepared by Westinghouse. The deflecting magnet is clearly shown in the upper left-hand portion, with the inlet tube and gas ionizing mechanism rising vertically above the pole pieces. The magnet is the 90° type, affording a shorter ion path, and since this reduces the number of collisions of the ions with the gas in the analyzer, somewhat higher gas pressures than usual can be tolerated. The use of a vertical ion source affords an experimental simplification in the ease with which new tubes can be sealed on and filaments can be replaced where necessary. Theoretical computations based on the instrument parameters indicate a resolution of 109, according to which the instrument should resolve mass 108 from mass 109.

The predictions are verified in representative analyses, which show as expected that the resolution is of this order. Typical curves taken on carbon dioxide show the three isotopes of oxygen, O^{16}, O^{17}, and O^{18}, and the two isotopes of carbon, C^{12} and C^{13}, which values are evident in curves showing a mass of 44, 45, and 46. Another test shows the mercury isotopes, Hg^{204} and Hg^{202}, which represent two mass units in 200 in the resolution expected from the geometry of the apparatus. The remaining mercury isotopes, which are only one mass unit apart, are not completely resolved. Very useful information has already been obtained with this instrument. Information is available in the literature for the following molecules: methane, ethane, acetylene, ethylene, propane, propylene, allylene, butane and isobutane, benzene, sulfur dioxide, carbon tetrachloride, chloroform, ammonia, carbon bisulfide, cyanogen, methyl alcohol, ethyl alcohol, nitrous oxide, bromine, hydrocyanic acid, carbon dioxide, carbon monoxide, water, hydrogen, oxygen, and nitrogen peroxide.

The sensitivity for analysis is expressed as the smallest amount of the least abundant component mass that can be detected in the presence of the most abundant component. One example may be mentioned. The instrument has been used to measure as little as 0.001 per cent of oxygen in nitrogen. The entire equipment is placed on a truck and the only outside connection required when the apparatus is in place is 110-volt alternating current and water connections for cooling the pumps. Further details are available in the Westinghouse publication, and it is a privilege to be able to present these meager details of an instrument, from which much important and useful information will undoubtedly be forthcoming in the near future.

APPLICATIONS. The vast program which has been in progress for some time on the separation and utilization of naturally occurring isotopes has been recorded in many places. Starting with the discovery of deuterium by Urey in 1932, there has been rapid progress in the separation or enrichment of other useful isotopes, such as Urey's methods for C^{13} from the more abundant C^{12} and also of N^{15} in quantities sufficient to make these substances available for biological tracer work (see also *223*). His methods (*137*) for enrichment based on the exchange principle have proved most useful (*268*, *273*). A typical example of columns for these studies is shown in Figures 190 and 191. Some examples of the use of these isotopes as tracers have been given by Rittenberg (*35*, *77*, *244*), and many others are currently recorded in the literature.



Courtesy, Eastman Kodak Co.

FIGURE 191. APPARATUS FOR SEPARATION OF ISOTOPES BY CHEMICAL EXCHANGE

Earlier investigations in the isotope field employed a great variety of methods, mostly refinements of density measurements, but at the present time the mass spectrograph despite its complication is regarded as the most reliable and accurate tool for the purpose.

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