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ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

A Division Membership Goal of 1000

PROBABLY very few of our readers realize that the Division of Analytical and Micro Chemistry is the youngest in the AMERICAN CHEMICAL SOCIETY. This honor we know will soon pass to a Division of Chemical Literature, but at least for the time being Analytical and Micro Chemistry is the baby of the Society, although it was organized in 1938. Prior to its formation, papers of an analytical nature were scheduled mainly by the Division of Physical and Inorganic Chemistry.

The Division of Analytical and Micro Chemistry is not only the most youthful segment of the Society's scientific groups but one of the most active.

One does not need to search very far to find the reasons for the present high degree of interest in the division. One is the administrative ability of the present officers and those who have guided its destiny in recent years. The other reason is the large number of active committees fostering the objectives of the division. In general, these committees are of two types. First, there is the group of administrative committees, such as the Nominating Committee, which are necessary to carry on the organization of the division and to promote its growth and well-being. The second group is devoted to furthering the purposes of the AMERICAN CHEMICAL SOCIETY in spreading the knowledge of chemistry and acquainting chemists with the current status of the field.

We feel that every analyst, whether or not he belongs to the Society and the division, should know about these committees, for they are all broadly laboring to improve the status of analytical chemistry and analytical chemists.

Executive Committee. W. A. Kirklin, chairman; G. T. Wernimont, vice chairman; W. G. Batt, secretary; P. J. Elving, 1948 chairman; M. L. Willard, 1947 chairman; J. R. Anderson, councilor, 1949–50; E. J. Hughes, alternate; H. C. Diehl., councilor, 1949; and R. M. Fowler, alternate. The chairman is associated with the Hercules Powder Co., Wilmington, Del., and the secretary, W. G. Batt, is with the Biochemical Research Foundation, Newark, Del.

Annual Symposia. B. L. Clarke, chairman, P. J. Elving, L. T. Hallett, I. M. Kolthoff, J. W. Stillman, E. Wichers, and H. H. Willard.

By-Laws. R. A. Burdett, chairman, C. M. Alter, and B. L. Clarke.

Microbalances. A. H. Corwin, chairman, H. K. Alber, A. A. Benedetti-Pichler, E. W. D. Huffman, P. L. Kirk, and L. B. Macurdy.

Papers. W. M. MacNevin, J. R. Churchhill, and A. O. Butler.

Speakers. J. F. Flagg, chairman, S. E. Q. Ashley, and F. R. Duke.

Nomenclature. L. T. Hallett, chairman, S. E. Q. Ashley, H. V. Churchhill, H. C. Diehl, N. H. Furman, and R. P. Graham.

Microchemical Apparatus. Al Steyermark, chairman, H. K. Alber, V. A. Aluise, E. W. D. Huffman, J. A. Kuck, J. J. Moran, and C. O. Willits.

Cooperation with Local Groups. H. F. Beeghly. Mr. Beeghly is associated with the Jones and Laughlin Steel Corp., Pittsburgh, Pa.

Membership. G. T. Wernimont, chairman, A. H. Bushey, W. W. Hilty, and Harry Levin. Mr. Wernimont is associated with the Eastman Kodak Co., Rochester, N. Y.

Every one of these committees is actively functioning. The officers of the division and the members of the various committees are looking to its membership and to analysts generally for suggestions on ways and means of increasing the activities of the division. Your cooperation is solicited.

The Division of Analytical and Micro Chemistry should have many thousands of members. The potentialities are there for such a membership. We ask on behalf of the Membership Committee that you become a member if you are not already one; next, that you bring in a new member in 1949. A plan as simple as that will bring the division to a membership of approximately 1000 by the end of this year.

Dues are only one dollar and should be sent to Secretary W. G. Batt, Biochemical Research Foundation, Newark, Del.

A strong active division is supporting the field of analytical chemistry, and the members of the profession who are giving so generously of their time to further our particular interests deserve to be encouraged by witnessing this year a large growth in the membership of the division.

What's Ahead

ANALYTICAL chemists will find the program for San Francisco (March 27 to April 1) of varied interest. Harry Levin of the Texas Company is chairman of a Symposium on Microchemistry in the Petroleum Industry, cosponsored by the Division of Petroleum Chemistry, while J. R. Matchett of the Western Regional Research Laboratory, Albany, Calif., is chairman of a Symposium on Analytical Chemistry in the Food Industry, in cooperation with the Division of Agricultural and Food Chemistry.

And it is not too early to remind our readers that the Annual Summer Symposium cosponsored by the Division of Analytical and Micro Chemistry and ANALYTICAL CHEMISTRY will be held in June at Wesleyan University, Middletown, Conn. The subject is "Organic Reagents," and the chairman is S. E. Q. Ashley of General Electric. G. M. Burford of Wesleyan is chairman of the Committee on Local Arrangements. More on the Annual Summer Symposium at a later date, but what is reported in these lines, plus the fact that analytical chemists will be flocking to the Pittsburgh Section's Analytical Symposium January 20 and 21 and Louisiana State's annual analytical get-together March 2 to 5, indicates busy and fruitful days ahead for the members of the chemical profession primarily interested in things analytical.

First Annual Review of Analytical Chemistry

IN RECENT YEARS great progress has been made in theoretical and applied analysis. Recognizing the need for bringing together in one place a record of these accomplishments, your editors laid plans many months ago for an annual series of reviews on analytical chemistry. Through the help and advice of many leaders in the field and much hard work by a group of outstanding authors, these plans have resulted in two groups of articles for the January and February issues. The first group, covering fundamental analytical developments, consists of 29 articles and occupies 171 pages. The second group, to appear in the February issue, consists of 11 articles covering the practical applications of analytical developments in various fields of specialization.

In these inaugural issues of an annual series, the authors have covered a five-year period to bring the subjects up to date and to lay a firm foundation for the future reviews, which will cover one-year periods.

We would like to take this opportunity to call attention to the outstandingly generous contributions of time and effort by the authors. It is only through their work and the cooperation of the organizations with which they are affiliated that these reviews are made possible. On our own behalf and for our thousands of readers, we express our sincere thanks and appreciation.

—*The Editors*

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January — FUNDAMENTAL ANALYSIS

Light Absorption Spectrometry. *M. G. Mellon*
Infrared Spectroscopy. *R. B. Barnes and R. C. Gore*
Raman Spectra. *W. G. Braun and M. R. Fenske*
Ultraviolet Absorption Spectrophotometry. *E. J. Rosenbaum*
X-Ray Absorption. *H. A. Liebhafsky*
X-Ray Diffraction. *H. S. Kaufman and I. Fankuchen*
Emission Spectroscopy. *W. F. Meggers*
Mass Spectrometry. *J. A. Hipple and Martin Shepherd*
Electron Microscopy. *C. J. Burton*
Light Microscopy. *E. E. Jelley*
Polarographic Theory, Instrumentation, and Methodology. *J. J. Lingane*
Organic Polarography. *Stanley Wawzonek*
Amperometric Titrations. *H. A. Laitinen*
Electroanalysis. *S. E. Q. Ashley*
Chromatographic Separations. *H. H. Strain*
Distillation. *Arthur Rose*
Extraction. *L. C. Craig*
Ion Exchange. *Robert Kunin*
Nucleonics. *C. L. Gordon*
Indicators. *I. M. Kolthoff*
Fluorometric Analysis. *C. E. White*
Instrumentation. *R. H. Müller*
Statistics Applied to Analysis. *Grant Wernimont*
Inorganic Microchemistry. *P. W. West*
Organic Microchemistry. *C. O. Willits*
Inorganic Gravimetric Analysis. *F. E. Beamish*
Organic Gravimetric Analysis. *J. F. Flagg*
Inorganic Volumetric Analysis. *C. J. Rodden*
Volumetric Analytical Methods for Organic Compounds, *W. T. Smith, Jr., and R. L. Shriner*

February — APPLICATIONS OF ANALYTICAL DEVELOPMENTS

Coatings. *T. G. Rochow and R. W. Stafford*
Essential Oils and Related Products. *Ernest Guenther and E. E. Langenau*
Fertilizers. *K. D. Jacob*
Food. *B. L. Oser*
Solid and Gaseous Fuels. *A. W. Gauger and H. T. Darby*
Ferrous Metallurgy. *H. F. Beeghly*
Nonferrous Metallurgy. *H. V. Churchill*
Petroleum. *Harry Levin*
Pharmaceuticals and Natural Drugs. *W. W. Hilty*
Natural and Synthetic Rubbers. *Norman Bekkedahl and R. D. Stiehler*
Water Analysis. *S. K. Love*

REPRINTS

Because these special review issues are likely to assume an important place in the literature of analytical chemistry and will be referred to again and again, plans have been made to issue a combined reprint of the January and February reviews. The reprints will be available about March 1 from the Reprint Department, American Chemical Society, 1155 Sixteenth Street, N. W., Washington 6, D. C. Price will be $1.50 per copy. Advance orders will be accepted.

LIGHT ABSORPTION SPECTROMETRY

M. G. MELLON

Purdue University, Lafayette, Ind.

THE general viewpoint of this review is substantially that adopted earlier (*36, 37*) for the preparation of a perspective of the subject. Thus, the subdivision of absorption spectrometry considered is limited to that part of the radiant energy spectrum capable of producing the sensation of light in the human eye. This visible region, covering a range of approximately 400 to 700 mμ for a normal observer, lies between the ultraviolet and the infrared regions.

For nonvisual measurements the operations of determining the absorptive capacity for radiant energy in the ultraviolet, visible, and infrared regions differ chiefly in the modification of instruments required to take care of the different properties of materials for the wave lengths represented by the respective regions. The visible region is unique in that, with visual instruments, the human eye is the receptor for the radiant energy unabsorbed by the sample. As materials absorbing selectively in this region are colored, one may be concerned not only with the qualitative and/or quantitative determination of the absorber(s), but also with the determination of the color as color.

The writer is substantially convinced of the soundness of the contention of physicists that the term "colorimetry" should be limited to this color measurement as such—that is, the specification of color in terms of equivalent stimuli. Then light absorptiometry would include the measurements for purely analytical purposes. Those made with comparimeters, such as the standard series and balancing types, would be relative in the sense that one simply matches the light absorptivity (intensity) of the unknown with that of a standard. Then those made with filter photometers and with spectrophotometers would be absolute in the sense that one determines the absorptivity in some numerical terms.

In view of the number of publications appearing during the period of this review, especially on applications, the writer has not tried to evaluate the contribution of each one. Instead, this summary represents an attempt to present what seem the most significant kinds of advances in the subject during the past few years. The outline conforms to the writer's current viewpoint on methods as a whole (*38*).

CHEMISTRY

By chemistry is meant here whatever is necessary in the way of preparative treatment to get a sample ready for the measurement. Included are familiar operations, such as dissolution, oxidation-reduction, pH adjustment, separation, complexation, coupling, and others.

Certainly one reason for the current popularity of light absorption methods is the possibility of dealing with elements, ions, radicals, and compounds. To handle all such constituents, as they are found in the vast number of natural and synthetic products and materials now known, is no small problem. In fact, time after time in a given analytical situation the stumbling block is lack of satisfactory reactions. One has to deal with the now known 96 chemical elements in their numberless combinations.

Whatever progress is being made in this chemistry seems to fall into fairly well defined categories.

New Reagents and Reactions. The search continues for specific reagents, the long-sought panacea for some of the analyst's difficulties. From the wealth of new organic compounds made annually there do come some new reagents and reactions. The extent of efforts thus far in this direction is shown by Welcher's new four-volume compilation (*59*), a part of which summarizes the use of organic compounds to prepare constituents for absorptiometric measurement.

Such new reagents, whether organic or inorganic, may provide a hitherto unavailable method (*7*). Much more often it means merely an additional method (*61*). In comparison to a reagent that is available, one is always concerned with possible advantages of the new substance, especially its general applicability and the degree to which it meets the requirements of an ideal reagent for this kind of work (*39*). Thus, the new reagent may provide more satisfactory performance for one or more items, such as range, stability, and freedom from interference.

Adaptation of Known Reagents and Reactions. In the effort to develop methods employing reagents meeting more nearly the ideal desired, various adaptations of well-known systems are proposed annually. Many examples might be cited.

Sometimes the adaptation of established reactions results in interesting indirect methods. Thus, the procedure of Scott and Johnson (*50*) for calcium rests upon the direct relation between the amount of the element and the extent of fading of excess permanganate solution following its reaction with the oxalate precipitated with the calcium.

Critical Study of Known Reactions and Reagents. The results of some critical studies in recent years with modern instruments seem to justify the prediction that many other methods would yield interesting data if investigated similarly. The information obtained leads to a better understanding of the nature and effect of the variable factors involved, with the resultant possibility of establishing the best compromise set of working conditions.

Rider's study (*47*) of an old method for the determination of the nitrite ion is an example. Various factors affect the diazotization and coupling reactions involved in the production of a measurable colored system. A reasonably workable procedure was evolved in the light of an understanding of the part played by several factors.

PHYSICS

Once the system is suitably prepared, measurement follows. This final operation is physics, because, by definition, measurement consists in finding the number of times the standard goes into the unknown.

Incidentally, all such measurement is instrumental, whether made with an analytical balance or a spectrophotometer. Current efforts to make the word "instrumental" include methods such as spectrophotometric, as opposed to gravimetric seem entirely unjustified, for instrumental is an inclusive, rather than an exclusive, term.

Under the subject of physics we may consider certain new definitions, new instruments, improvements in old equipment, and means for checking instruments.

Definitions. The confusion in usage of terms, symbols, and data in absorptiometry remains unsurpassed by that in any other division of quantitative analysis.

The results of the first recent effort to achieve uniformity are contained in the comprehensive, scholarly report of the colorimetry committee of the Optical Society of America (*29*). The recommended usage had a foundation, of course, in the colorimetry report of 1922 (*54, 55*) and the spectrophotometry report of 1925 (*25*). The new recommendations set the standard, especially for certain word endings and definitions.

The second recent effort to provide uniformity of practice is that of the National Bureau of Standards (*42*). These recommended definitions and symbols were agreed upon by eleven divisions or sections in the bureau for use in its publications. In general, the definitions of the colorimetry committee of the Optical Society of America are retained for words such as radiant energy, radiation, light, transmittance, and transmittancy. Reference should be made to (*42*) for details. However, certain items on symbols may be noted especially as they apply to the measurement of solutions in absorption cells.

In Figure 1, let I_1 represent the radiant energy incident upon the first surface of the sample cell, I_0 that entering the solution, I that leaving the solution and incident upon the second surface, I_2 that leaving the sample cell, b the length of the absorbing path between the boundary layers of the solution, and c the concentration of solute or desired constituent in the solution. Then, for the transmission of homogeneous radiant energy through a homogeneous, isotropic, nonmetallic medium having plane, smooth, parallel faces,

$T = I_2/I_1$ = transmittance of sample
$100T$ = percentage transmittance
$T_i = I/I_0$ = internal transmittance of sample

The terms of most concern to the quantitative analyst relate to the rectilinear transmission of homogeneous radiant energy through a homogeneous, isotropic, nonmetallic medium such as a liquid, solution, vapor, or gas confined between the windows of a cell.

Let $T_{\text{soln.}}$ represent the (over-all) transmittance of a given cell containing a solution or homogeneous mixture of liquids or gases, of which the desired constituent is the solute or one constituent. Let $T_{\text{solv.}}$ represent the (over-all) transmittance of the same or duplicate cell containing pure solvent, or the same mixture in the same relative proportions minus the desired constituent.

$T_s = T_{\text{soln.}}/T_{\text{solv.}}$ = transmittancy of sample
$100T_s$ = percentage transmittancy
$A_s = -\log_{10}T_s = \log_{10} 1/T_s$ = absorbancy of sample (this replaces optical density, D, or extinction, E)
$a_s = A_s/bc$ = absorbancy index of material (this replaces extinction coefficient, k)
a_m = molar absorbancy index, c being expressed in moles per liter and b in centimeters (this replaces molar extinction coefficient, K or ϵ)

This circular ignores the absorption coefficient, k', involved if the logarithmic base is e, and no term is assigned to the quantity $a_sc(= A_s/b)$.

Instruments. The design and development of instruments fall, of course, in the domain of physics and engineering. However, in view of the chemist's compelling interest in applications, brief mention of such progress is justified.

As in the case of reagents and reactions, this interest centers in new items and in modifications and improvements of old ones. These may be considered in terms of kinds of instruments.

COMPARIMETERS. The general utility of comparimeters, even of the simplest types, remains unquestioned for a wide variety of purposes. Current enthusiasm for gadgetry should not be allowed to obscure the generally commendable objective of doing a thing as simply as possible. Perhaps the chief development worth mention in this class is the adaptation of balancing instruments for work on a micro scale.

FILTER PHOTOMETERS. Through the period under review the popularity of filter photometers, especially photoelectric instruments, has increased rapidly. Industrial analysts report an ever-increasing number of determinations each year made by this means.

Instrumental progress has been chiefly in the direction of improvements. Two examples may be cited for the filters used. The first, which concerns the filter itself, is the new type of interference filter (*8*, *22*). Although these are still relatively expensive, if one gets a set of, say, a dozen, they do provide narrow spectral bands, as filters go. The location of this band can be reasonably close to the desired median wave length. Thus, the writer asked for one centering at 525 mμ; measurement showed the peak at 528 mμ, with a transmittance of 32.5%, and a width of 16 mμ at the half-way height of the band. Very recently continuously variable interference filters have been described by Turner and Ullrich (*57*).

The second example is the provision for rapid change of filters in the Kromotrol instrument (*60*). Ten glass filters, with maximum transmittances at 400, 430, 460, 490, 525, 565, 620, 650, 700, and 730 mμ, are arranged around the light source in the form of a turret which can be rotated to bring the desired filter into the beam.

Cooper (*16*) has discussed the problem of selecting the proper filter to be used with a specific colored solution, light source, and light-sensitive element.

Comar (*14*) has suggested an indirect calibration of such an instrument by means of spectrophotometric measurements.

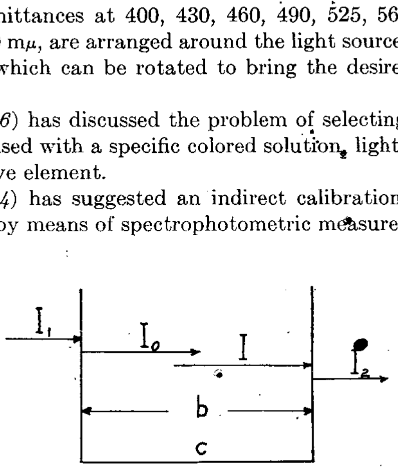

Figure 1. Schematic Representation of Transmission of Radiant Energy

SPECTROPHOTOMETERS. The simplest of the new spectrophotometers are the new models of the Coleman Junior (*12*) and the No. 14 Universal (*13*). Accessory equipment provides for fluorometry with the latter model. These instruments seem to have had wide acceptance in preference to filter photometers. Presumably such choice may be attributed to the ease of isolating the desired spectral band by turning a dial instead of changing filters. If this band is 35 mμ wide, obviously the filter mentioned will isolate a band less than half as wide, an advantage, if such resolution is necessary.

The instruments mentioned all represent commercially available equipment. Of the instruments assembled during the period under review, that described by Zscheile (*62*) seems to be capable of highest precision. Built around a Müller-Hilger double quartz monochromator, the total assembly is a superb example of meticulous instrumentation, capable of operating on a very narrow spectral band width. In addition to standardization work, it is an excellent instrument for work with multicomponent systems.

As examples of improvements for facilitating the use of established instruments, four papers may be cited. Coor and Smith (*17*) described the means used to make the Beckman quartz instrument a recording type. Improved resolution is claimed for the adapted instrument, with little loss in accuracy of transmission measurement. A fluorometric attachment has been devised for this instrument (*23*).

The Beckman glass spectrophotometer, just announced (see Figure 2), represents a simplification of the Model DU quartz instrument (*40*). The use of a glass Féry dispersing prism reduces the cost, but restricts the measurable range, compared to that possible with quartz optics. Where the smaller range and the somewhat wider spectral band width passed are unobjectionable, the cheaper instrument should provide high grade performance, so characteristic of the more versatile model.

No longer may the General Electric photoelectric spectrophotometer be referred to as "the" recording spectrophotometer. The new Cary instrument (*4*), equipped with multiplier photocells and various other devices (see Figure 3), seems to possess some of the combined advantages of General Electric recording, with Beckman precision and range. Unfortunately, the writer cannot offer personal experience with it.

Following years of experimentation, two papers describe improvements and adaptations of the General Electric instrument.

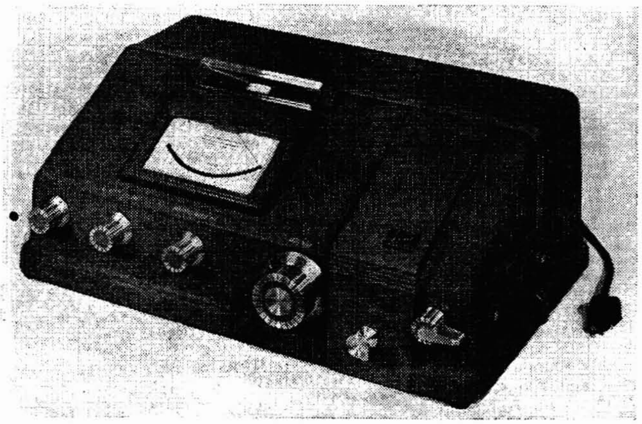

Figure 2. General View of Model B Beckman Spectrophotometer

The first publication, by Kienle and Stearns (*31*), concerns 23 modifications.

> (1) A rotating skein holder; (2) a cam to plot the function, $\log[(1 - R)^2/R]$, in which R is the reflectance; (3) a magnified wave-length plot; (4) a magnified function of transmittancy plot; (5) a microtransmission sample holder; (6) an optical stop in the monochromator; (7) a cam to plot $\log \log 1/T_s$, in which T_s is transmittancy; (8) a calibration-filter positioning device; (9) a wave-length clutch; (10) an optical rotation sample holder; (11) a cam to plot $\log \alpha$, in which α is the angle of optical rotation; (12) a cam assembly permitting quick selection of cams; (13) a recorder-drum time device; (14) oblique incidence sample holders; (15) retardation-plate flickering in the photometer; (16) an extended wave-length range; (17) a sliding cover for the transmission chamber; (18) variable plotting speeds; (19) a pen drive free of backlash; (20) a sample holder rejecting the specular component; (21) a horizontal sample holder; (22) retardation-plate polarization mixing of the photometer light; and (23) a black mask for absorbing specular reflectance of flat samples.

These modifications were helpful in cases such as (1) chemical analysis of reactions on fibers; (2) chemical identification in solution; (3) determination of reaction rates; (4) determination of refractive index and absorption coefficient of inks; (5) chemical analysis by transmission; (6) measurement of crystal structure; and (7) colorimetry of chemicals.

The second paper on this instrument, by Richardson (*46*), deals with certain techniques and accessories for facilitating its application. They relate to the following items, among others:

> (1) Placing the graph paper; (2) checking the wave-length scale; (3) cooling the light source; (4) an air-drying unit for the amplifier; (5) a modified integrating sphere for transmittance and reflectance measurements; (6) aluminum supporting plates for the magnesium oxide surface; (7) specular light traps; (8) modified lens system for special measurements; and (9) an extension of the wave-length range.

The problem of intercomparison of work from different laboratories is discussed by Ewing and Parsons (*21*). This comparative study involved ten Beckman instruments using a potassium hydrogen phthalate solution for measurements at 264 and 281 mμ. Still more recently Tunnicliff (*56*) suggests the use of line sources as a means of making the conditions of such measurements somewhat more reproducible. As for this idea, a more elaborate line source assembly for the König-Martens instrument at the National Bureau of Standards was described much earlier by McNicholas (*35*).

Extension of the range of concentrations measurable spectrophotometrically is illustrated by the work of Kirk, Rosenfels, and Hanahan (*32*) using capillary absorption cells. This meticulous work is claimed to yield much higher sensitivities with colorimetric work than are otherwise attainable.

The general question of accuracy and precision in such measurements, as well as the applicability of Beer's law, is still being discussed, as illustrated by the papers of Körtum (*33*), Citerne (*10*), and Savost'yanova (*49*).

REFLECTOMETERS. The General Electric spectrophotometer has been especially useful for the determination of the reflection characteristics of materials, such as ceramic ware, paper, and textiles. If the reflectance curve itself is not adequate, it does serve as the basis for the calculation of the International Commission on Illumination trichromatic coefficients.

Simple, inexpensive instruments which would give directly something approximating these values are obviously desirable, in view of the expense of the General Electric instrument and the time required to make the necessary calculations. Hunter's reflectometer (*27*) is an example of such a photoelectric tristimulus colorimeter.

Series of standards, having specified reflectance values, are now available from the National Bureau of Standards (*30*).

APPLICATIONS

If one may accept the obsession of the average "Uesanian" (*5*) that numbers measure importance, the kind of determination included in this review seems to rank first. According to the survey of Strong (*53*), the colorimetric and spectrophotometric methods, combined as absorptiometric, constitute 28.7% of the total for the period of his survey. Although some ultraviolet and infrared methods probably fall in his spectrophotometric group, the figure is still impressive. His survey, of course, did not include papers on color specification.

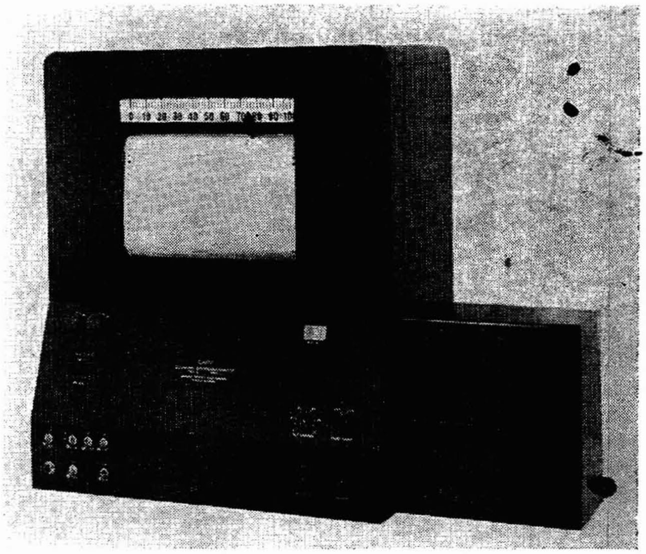

Figure 3. General View of Model 10 Cary Spectrophotometer

Chemical Analysis. The hundreds of total papers are not easily summarized. The bibliographies of Stillman (*51*) and of the Central Scientific Co. (*9*) are limited selections, the individual items being largely papers appearing in ANALYTICAL CHEMISTRY.

Several books represent the results of efforts to bring together methods for certain kinds of materials. Sandell's critically selected compilation (*48*) deals first with the general principles of methods and then with procedures for traces of metals. Haywood and Woods' book on metallurgical analysis (*26*) is limited to the systematic absorptiometric analysis of certain alloys by means of the Hilger absorptiometer. For the first time a section on photometric principles and methods for selected elements is included in the last edition of the standard methods of the American Society for Testing Materials (*3*).

More general types of compilations are illustrated by the monograph of Lange (*34*) and by the treatise of Snell and Snell (*52*). The three volumes of the new edition of the latter work summarize the present status of instruments and then follow hundreds of presumably workable methods for the determination of constituents in inorganic and organic materials.

In addition to the specific kinds of items mentioned as developments under chemistry, the general nature of contributions in individual papers may be summarized under items such as the following: (1) new methods for many constituents; (2) improvements in old methods involving an understanding and control of both chemical and instrumental factors, thus helping to make the over-all procedures more workable and reliable; and (3) adaptation of old methods to specific materials, especially for systematic analysis. The last point is well illustrated by the inclusion of colorimetric methods for over twenty constituents in the last edition of the A.P.H.A. standard methods for water analysis (*2*).

Multicomponent determinations, involving the use of simultaneous equations, as in Weissler's method for titanium, vanadium, and molybdenum (*58*), may be facilitated by computation aids, such as those of Fred and Porsche (*24*), or by the more elegant electrical calculators (*15*, *19*).

The use of spectrophotometric curves as a means of qualitative interpretation of color changes in materials is well illustrated by the work of Clark *et al.* (*11*) on quenching oils.

Ayres (*6*) has directed attention again to the merit of plotting calibration curves on the basis of the recommendations of Ringbom.

Color Specification. Just as the metallurgist is concerned with the elements that will contribute to the hardenability of steel, their amounts, and the degree of hardness obtained on suitable treatment, the absorptiometrist is concerned with what gives a material its color, the amount of the constituent, and the color imparted. Determination of the nature of the constituent and its amount constitutes the role of analytical chemistry. Description and specification of the color are included by the physicist's definition of colorimetry.

Although the use of words for this purpose is probably as old as language itself, names such as elephant's breath leave something to be desired in the way of clarity and accuracy. Some increase in use of the ISCC-NBS system is evident, as in Pearce's book on qualitative analysis (*44*). The past decade has brought marked developments in the direction of objective specification. Thus, a recent pamphlet of the Du Pont Company on traffic paints (*18*) gives, in addition to samples of the colors (in three-color printing), specifications in terms of the material standards of the Munsell (*41*) and the Ostwald (*28*) systems, and the I.C.I. trichromatic coefficients (*29*).

New combinations of material standards for specification by color matching continue to appear. A recent example is the set of Plochère (*45*).

The work of Osborn and Kenyon (*43*) on the color of rosin is a good example of the problems chemists encounter in the application of the spectrophotometer in color studies.

The continued and increasing technical importance of color problems in specific industries is indicated by symposia on color held by the Technical Association of the Pulp and Paper Industry (*54*) and by the American Ceramic Society (*1*). The papers presented give a comprehensive, general statement of the contemporary situation.

Special mention should be made of the new book by Evans (*20*) on the general aspects of color and its measurement and interpretation.

MISCELLANEOUS ITEMS

Several items seem of more than passing general interest to those concerned with the broad aspects of the analytical measurement of colored systems.

The reviewer finds the *News Letter* of the Inter-Society Color Council indispensable as a means of keeping in general touch with color developments.

During 1948 the *Spectrophotometry Digest* appeared as a publication of the Special Products Division of the Apparatus Department of the General Electric Company. Although some items are of interest only to users of the General Electric instrument, others, such as nomographic charts, are of general interest.

In the summer of 1948 a course on color measurement, with laboratory work on spectrophotometers, was conducted at Union College under the auspices of the General Electric Company. In addition to speakers from the company, the staff included such well-known men as S. Q. Duntley, E. I. Stearns, D. L. MacAdam, and A. C. Hardy.

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INFRARED SPECTROSCOPY

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AT THE time of the installation of the first industrial infrared spectrometers during 1936–37, little was it realized to what uses the field of infrared spectroscopy would be put or to what extent it would become accepted as an industrial tool. Under the pressure of the war years, however, industry found so many applications for infrared, particularly in connection with the petroleum and synthetic rubber programs, that its merits were demonstrated repeatedly and its place as an important tool for research, analysis, and control was assured. In direct response to the demands of industry spectrometers were made available commercially and in large numbers. These instruments have resolving powers comparable to most of the academic research spectrometers and have the additional features of convenience, stability, and uniformity.

The commercial availability of these spectrometers has made possible the adoption of infrared by many industrial laboratories which deal with a wide variety of organic chemicals other than hydrocarbons and also by university laboratories interested only in organic research rather than in infrared spectrometry itself. Infrared has now become a research tool widely accepted by chemists and no longer remains only a branch of the broad field of spectroscopy practiced by a small group of physicists. The techniques and uses of infrared are now taught in a great many universities and colleges rather than in a limited few as was the case prior to its recent popular acceptance.

As is to be expected, several publications of a general nature have appeared since 1936 which serve to document this expansion. A small book covering general applications, published in 1943 by Barnes, Gore, Liddel, and Williams (*20*), included a bibliography of 2701 previously published papers. Herzberg's classical volume on "Infrared and Raman Spectra of Polyatomic Molecules," including over 900 references (*140*), appeared in 1945. Mathieu in France has written a comparable volume (*190*). A conference on spectroscopy at the Museum of Science and Industry held in Chicago during 1944 (*233*) included many papers of interest. In 1945 the Faraday Society held a Symposium on the Application of Infrared Spectra to Chemical Problems (*279*) with 19 timely papers. The American Petroleum Institute in collaboration with the National Bureau of Standards has collected from various research workers and made available through its Research Project 44 over 700 spectra of hydrocarbons and related substances. This project is continuing.

The Ohio State University has sponsored interesting and valuable symposia on infrared spectrometry and directly related subjects during June of 1946, 1947, and 1948. At the last of these symposia, which have rapidly become the outstanding yearly event in the field of infrared, some 330 persons were in attendance. At these meetings discussion is lively and ideas are interchanged freely between individual and groups. Publication of the papers presented is left to the individual authors, and no attempt is made to collect them in one volume.

The Optical Society of America has also conducted important symposia in the field, and the abstracts of the papers have appeared in its journal (*208, 209*).

Preparation for the writing of this present review revealed some 1000 papers published since 1943 review article (*20*). No attempt can be made here to refer to each of these papers. On the contrary, only those are cited which serve to show the major trends in the various phases of this rapidly expanding field.

INSTRUMENTATION

A comprehensive review on instrumentation and experimental techniques was published recently by Williams (*291*). This paper covers the history, techniques, and applications as well as the advances in instrumentation in the very near infrared from 13,300 to 4000 cm.$^{-1}$, the near infrared from 4000 to 400 cm.$^{-1}$, the far infrared from 400 to 30 cm.$^{-1}$, the microwave region, infrared filters, and gas analyzers as well as many miscellaneous applications of infrared radiation. With its 210 references, this review is required reading for anyone interested in this phase of infrared.

Since 1943, if one excepts the general commercial availability of suitable spectrometers, the major trends in instrumentation have been the following:

The substitution of breaker type direct current amplifiers (*180, 236*) in place of galvanometers or photorelay amplification. This introduction of a satisfactory and commercially available amplification system capable of handling the small energies obtainable from spectrometer receivers has enabled the almost universal use of fountain pen type recorders.

Interrupted beam alternating current amplification systems introduced to eliminate the bothersome zero drift encountered in direct current systems (*179, 236*).

A persistent demand for infrared spectrophotometers or direct reading percentage transmittance spectrometers has been met by the Baird Associates (*12, 205*) and The Perkin-Elmer Corporation in this country and by Adam Hilger (*121*) in England. Several other spectrophotometers have been described (*17, 173, 188, 231, 299, 300*). This trend is undoubtedly in the right direction; however, there still remain many instrumental problems which must be overcome before these spectrophotometers are accepted universally.

Major improvements have been made in the field of radiation detectors, such as vacuum thermocouples of higher sensitivity and better construction (*118, 143, 179, 243*). Photoconductors sensitive to short wave-length infrared, such as thalofide cells and lead sulfide cells, were developed for military purposes and have only recently been applied to spectrometers (*38, 247, 256*). Such detectors should become increasingly useful.

DISPERSING SYSTEMS

As yet few laboratories engaged in analytical research (*206*) have employed spectrometers equipped with diffraction gratings. Whereas the earlier spectrometers were equipped almost exclusively with sodium chloride prisms, it is now possible to obtain prisms of the following materials: sodium chloride, lithium fluoride, synthetic fluorite (CaF_2), potassium bromide, and a mixed crystal of thallium bromide–thallium iodide called KRS-5 (*23, 24, 70, 123, 146, 215–217, 272, 280, 297*). Each of these materials has a definite function and with KRS-5 the useful range of prism spectrometers has been extended to about 250 $cm.^{-1}$ (40μ).

OSCILLOGRAPHIC RECORDING

Following the original publication of Baker and Robb (*17*) in 1943, both Sutherland (*77–79*) and Thompson (*160, 269*) in England have described spectrometers employing cathode ray oscillographic recording. This technique should ultimately be of considerable use in following the course of certain chemical reactions in short spectral intervals.

CELLS, WINDOWS, AND OTHER ACCESSORIES

The necessity for using soluble halide cell windows has for a long time limited the application of infrared spectroscopy to samples essentially of a nonaqueous nature. Several halide cells have been described recently (*44, 57, 120, 207*)) but the simple cell developed by Colthup (*62*) appears to offer one of the most feasible solutions to the cell problem. Silver chloride windows offer good transparency (*7, 105, 147, 165*) and low solubility. They are, however, not the ideal window material because of their reactivity, ductility, and the difficulty encountered in repolishing them. Eastman Kodak has produced a glass (EK No. 25) which shows excellent transmission from 300 millimicrons to about 4.5 microns. This glass, however, cannot be worked in the same manner as ordinary glass.

One of the prime disadvantages of the Nujol mull technique—namely, the obscuring of the C—H absorption bands—may now be eliminated through the use of perfluorokerosene (Du Pont).

The reduction of the effect of scattered radiation in spectrometers is now regularly accomplished by the use of filters, powder filters (*136*), or echelette gratings (*290*).

Using cells of silver chloride plates, Barnes, Gore, and Peterson (*122*) have explored the field of aqueous phase infrared. As solvents D_2O, DCl, and NaOD along with their hydrogen analogs were successfully used.

POLARIZED RADIATION

Pfund (*214*) has recently improved his original selenium reflection method for polarizing infrared. Elliott, Ambrose, and Temple (*92–94*) have described a transmission polarizer using their selenium filters, and Halford (*202*) and Wright (*296*) have discussed silver chloride transmission polarizers. These are important developments and there is now no reason why the use of polarized infrared should not be accepted widely for the study of the orientation of infrared active groups in crystals and other solid phase samples.

GAS ANALYZERS

An important development, from the industrial point of view, is the introduction of infrared gas analyzers which employ no dispersing systems (*96, 186, 298*). These instruments are in general very sensitive and are capable of detecting selectively as little as a few parts per million of many gases or vapors which exhibit strong infrared absorption. The simplicity and ruggedness of these devices make them very useful for obtaining continuous analyses of gas streams and also for control purposes. In general, they may be classed either as the positive (*46, 186*) or the negative filter type (*298*). Luft in Germany (*186*) constructed a positive filter type which is now being manufactured in England. Practical instruments of the negative type are sold by Baird Associates. The use of such gas analyzers should increase.

EMISSION SPECTRA

In this field an interesting paper by Kapff (*154, 155*) showed that thin films of organic liquids when heated emitted characteristic spectra, whereas the emission from heated thick layers was largely of the gray body type. Simard *et al.* (*246*) showed the use of emission spectra in studying reactions such as the thermal decomposition of ethylene oxide.

QUALITATIVE ANALYSIS

Undoubtedly, the widespread acceptance of infrared as a research tool is based primarily upon the speed, accuracy, and uniqueness with which chemical analyses can be performed through its use. Practically each issue of the journals presents the details of still another analytical problem which has been solved by infrared means. In this group are some which are solvable by no other means and many in which the application of infrared has made possible material savings in time or substantial increases in accuracy.

Each of the individual spectra in literally hundreds of papers contributes to the general fund of data available for qualitative analyses. Unfortunately, space does not permit of a complete bibliography. General papers discussing the application of infrared spectroscopy to qualitative analyses have recently been published by Barnes *et al.* (*19–21*), Thompson (*261–266, 270*), Sutherland (*255, 258*), Jones (*152*), Coggeshall *et al.* (*55, 238*), Brattain (*43*), Naylor (*201*), Luft (*185*), and Lecomte (*168, 169*). These treat the methods of sample preparation, positions of known absorption bands, and interpretation of the spectra.

The use of infrared in the identification of specific classes of compounds has been discussed in many papers. The most complete collection of spectra of any one class is the American Petroleum Institute Project 44 on hydrocarbons referred to above. Among the classes of compounds studied are: conjugated double bond systems such as di-, tri-, and tetraenes, azines, and furals (*40*), nucleic acids (*39*), methylcyclopropanes (*27*), penicillins (*22, 112*), deuterated benzenes (*8–11*), orthosubstituted cyclohexanones (*51*), urinary ketosteroids (*87, 108–111*), disubstituted benzenes (*82, 85*), Pennsylvania lubricating oils (*139*), synthetic rubber (*25, 61, 97, 144*), the carbonyl stretching vibration in steroids (*151, 153*) and in ketones (*50*), drying oils (*164*), amino acids and their complexes (*163, 174–177*), polyalkylene sulfides (*189*), alkylphenols (*161*), cyclopentanes and cyclohexanes (*218*), tocopherols and related molecules (*237*), fatty acids (*226*), octenes dienes, and mono-olefins (*227–230*), dicarboxylic acids (*242*), indoles (*249–251*), useful infrared solvents (*278*), organosilicon polymers (*301*), and cresols, xylenols, and cresylic acids (*287*). Other papers by Sutherland, Thompson, and Lecomte contain useful spectra on molecules.

Those using infrared spectra for analytical purposes face a real problem in their efforts to keep up with the published results of others and to keep these results in ready reference form. As a step in this direction several important articles have appeared on the use of punched card systems (*254, 277*). At the last Ohio State Conference a committee was formed with E. Carrol Creitz of the Bureau of Standards as chairman.

QUANTITATIVE ANALYSIS

The wartime use of infrared for rapid quantitative analysis by the petroleum and synthetic rubber industries is largely responsible for its present popularity. As might be expected, many of the published papers on quantitative analysis are in these fields. General articles in which methods and procedures for performing quantitative analyses are outlined have been published by Brittain (*43*), Beckman (*31*), Kent and Beach (*158*), Coggeshall and Saier (*58, 238*), Corin (*71*), Fry, Nusbaum, and Randall (*104*), Seyfried and Hastings (*244*), Thompson (*261*), Sutherland (*255, 258*), White *et al.* (*135*), and Barnes *et al.* (*20, 22, 25*).

Among the more specific papers may be cited: a procedure for determining trace impurities in iso-octane (*4*), low temperature analysis of octane mixtures (*6*), crystalline penicillins (*22, 112*), synthetic and natural rubber mixtures (*25, 86*), the analysis of gas streams for butadiene content (*298*), an analysis of the five isomers of 1,2,3,4,5,6-hexachlorocyclohexane (*76*), DDT (*89*), olefins in gasoline (*150*), specific hydrocarbon analyses (*41, 42, 137, 156, 170, 220–223, 235, 276, 286*), ortho, meta, and para isomers, and iso- and thiocyanates (*156, 289*).

Gas analyzers have been applied quantitatively for the analysis of toluene-benzene mixtures (*106*), an optical acoustical method (*46, 282*), and for butadiene and styrene in plant gas streams (*298*).

Several important papers have appeared with aids and techniques related to quantitative analysis but not reporting specific analyses. Among these are: an automatic simultaneous equation computer (*1, 35, 63, 103, 133, 145, 198, 199, 240*), electrical and mechanical methods of plotting percentage transmission against wave length (*36, 107, 232, 292*), a calibrated null circuit for Perkin-Elmer spectrometers for obtaining optical densities or percentage transmissions (*49*), an interference method for determining cell thicknesses (*248*), and an alternate method for cell thickness determinations (*259*).

The influence on quantitative analyses of pressure broadening and of failure to obey Beer's law has been discussed in detail by several investigators (*59, 60, 88, 98, 99, 172, 204, 241*).

HYDROGEN BONDING

Always a popular subject, the use of infrared for studying inter- and intramolecular bonding in various molecules continues. In connection with these studies in crystals and other solid state samples polarized infrared has played an important role. Among the important articles on this subject are: a study of the stereochemistry of the hydroxyl group in vinyl alcohols (*45*), hindered and unhindered phenols (*56*), a method for differentiation between inter- and intramolecular linkages in the near infrared (*90*), infrared dichroism in dibasic acids and nylon films (*114, 116*), three types of O—H frequencies and the role of double bonds in chelation (*101, 102*), association in alcohols (*74, 75, 80, 142*), the effect of bonding on the carbonyl frequencies (*171*), crystals containing hydroxyl groups (*181–184, 187*), the broadness and other characteristics of association absorption bonds (*213*), a theoretical discussion of spectra and bonding (*191, 219*), evidence for the NH—N bond in ethyleneimine (*267*), a review of bonding and vibration spectra (*281*), intensity measurements of the OH bond in the near infrared (*283*), and a method for detecting interaction in the near infrared (*302*).

THEORETICAL AND MOLECULAR

Structure Studies. As might be expected from the greater over-all activity in the field of infrared, interest in the vibrational analysis of molecules is on the increase. Because of their simplicity and general utility the hydrocarbons have received the bulk of the study, although several other molecular types have attracted attention.

In connection with benzene and its derivatives the following studies have been reported: the potential function of benzene (*13*), combination bands and molecular symmetry (*18*), bond torsion in the vibrations of the molecule (*32, 91, 128*), the vibrations of benzene derivatives and the Class A carbon vibrations of toluene (*33, 52*), the theory of the electronic structure of conjugated systems (*73*), the shift of an aromatic band near 815 cm.$^{-1}$ in substituted benzenes (*124*), the normal coordinates of a monosubstituted benzene molecule (*113*), the size and vibration frequency of the excited benzene molecule (*125*), the spectra of benzene in the solid liquid, and vapor states (*129*), some benzene molecules containing isotopic carbon atoms (*82–85*), the nonplanar vibrations and those of p-benzene-d_2 and p-benzene-*dx* (*141, 195, 196*), and a series of papers by Ingold and his coworkers (*8–11, 141, 148, 149*) on benzene and its deuterated forms.

In the hydrocarbon field the following references are of interest (*3, 5, 14, 26, 30, 33, 47, 54, 60, 72, 91, 95, 100, 159, 166, 167, 178, 192, 194, 200, 245, 252, 253, 257, 260, 268, 284, 285*).

Other studies of interest include ozone (*2, 117, 295*), hexafluoroethane (*212*), methyl halides (*15, 16*), nitric acid (*28*), ammonium chloride and bromide (*29*), uranium hexafluoride (*37*), Rochelle salts (*48*), ionic crystals such as orthorhombic carbonates (*64–69*), hydrogen sulfide (*127, 293*), halomethanes (*34, 81*), the use of polarized radiation in the structural analysis of long-chained polymers (*93, 115, 116*), alcohols, ethers, and amines (*119*), ketene (*132, 134, 197, 288*), acrylonitrile (*131, 271*), carbon dioxide (*138*), fluoroform (*34*), urea (*157*), pyridine (*162*), ammonia in the pure rotation and microwave regions (*203*), the potential barrier-hindering rotation of dimethyl sulfide (*210*), simple fluorocarbons (*34, 211, 212*), 1,2-dichloro- and dibromoethanes (*126*), dioxane and trioxane (*224, 225*), the force constants of certain OH and NH linkages (*234*), and the active frequencies of quartz (*239*).

General papers of unusual interest include those by Cleveland and Meister on the use of group theory (*53, 193*), Halverson's review on the use of deuterium in spectroscopy (*130*), Halford's studies on the condensed phases (*47*), and Wilson and Thorndike's series on band intensities (*273–275, 294*).

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RAMAN SPECTRA

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IN THE 20 years since its discovery, the Raman effect has provided new approaches for studying molecular structure, the thermodynamic properties of materials, reaction kinetics, and the qualitative and quantitative analysis of natural and synthetic products. This paper is a brief review of the current literature relating to the application of this phenomenon to analytical chemistry. This review covers chiefly the period from 1943 to the present, although some earlier work is included.

The theory and application of the Raman spectra have been rather well covered in several monographs on the subject. Particularly good are the books by Herzberg (*29*), Hibben (*30*), Kohlrausch (*33*), and Sutherland (*69*). The paper by Glockler (*21*) brings the work in Hibben's monograph to July 1942. Goubeau (*23*) has written a review on the analytical applications of the phenomenon which covers the work to 1939 very well. The paper by Stamm (*67*) gives a brief but good discussion of the theory.

APPLICATIONS

The variety of problems to which analytical Raman spectroscopy has been applied demonstrates the versatility and usefulness of the method, and, incidentally, often the ingenuity of the investigators. In cases where the constituents of the material being examined are known qualitatively and where the spectra of the individual compounds present are available for comparison, the analysis is usually straightforward. However, when the spectra of the components are not available, or when the materials are of unknown molecular structure, the analysis becomes complicated. This is often the case in the study of natural products, and usually the best that can be done is to compare the spectrum of the unknown with those of structurally similar compounds. Most of the current applications are in the field of organic chemistry, particularly hydrocarbon mixtures.

The earlier work on the analysis of petroleum products has been outlined by Hibben (*30*), Glockler (*21*), and Kohlrausch (*33*), previously cited. Some review papers which have described the field of usefulness of the method in relation to other physical methods of analysis are by Nielsen (*41*), Naylor (*39*), Schlesman and Hochgesang (*59*), Adrianov (*1*), Baroni (*2*), and Shorygin (*62*). More specific data on the method as applied to petroleum mixtures are given by Bazhulin (*3*) who presented the results of a semiquantitative analysis of a number of petroleum mixtures by the comparison with standard samples, and by Gerding and van der Vet (*19*) who applied the method to the analysis of binary and ternary mixtures of pentenes. Shorygin (*61*) studied the composition of light motor fuels containing benzene, toluene, cyclopentane, cyclohexane, cyclohexene, pentenes, and octane isomers. Vol'kenshteĭn *et al.* (*73*, *74*) analyzed Baku, Grozny, and Syzran natural gasolines and several cracked gasolines with the aid of Raman spectra. Midzushima *et al.* (*37*, *38*) determined the constituents of several Sanga-Sanga and north Sumatora gasolines. Delwaulle, François, and Weimann (*11*) and Okazaki (*43*, *44*) analyzed several fuels prepared by the Fischer method using the Raman technique. Rank, Scott, and Fenske (*53*) outlined a method using an internal intensity standard and applied this to the analysis of hydrocarbon mixtures. Rosenbaum, Martin, and Lauer (*58*) report a procedure for analyzing four-component aromatic mixtures using known blends as standards. Fenske *et al.* (*15*), using a recording photoelectric spectrograph developed by Rank and Wiegand (*54*), gave the analyses of several four-, five- and six-component hydrocarbon mixtures and showed how the photoelectric method could be applied to analytical work.

Glacet (*20*) studied the reduction products of crotonaldehyde with magnesium and acetic acid and, by means of Raman spectra, showed that the products contained an ethylenic linkage but gave no indication of the presence of a carbonyl group. Pajeau (*45*) applied the Raman effect to the analysis of a mixture of dibromobutanes in his study of catalytic dehydrogenation in the presence of beryllium sulfate. Chiurdoglu (*7*), in examining the ring enlargement of *cis*- and *trans*-1,2-dialkylcyclopentanes by aluminum chloride, used Raman spectra to analyze the reaction products, and showed that they are transformed into cyclohexanes and paraffins. Ducasse (*13*), in his work on the action of propanol on sodium ethylate, identified the unsaturated compounds and showed that *cis-trans*-ethylene structures were present in the reaction product. David, Dupont, and Paquot (*10*) hydrogenated cyclopentadiene and its dimer and identified, using Raman spectra, the reaction products as cyclopentene and cyclopentane. Pajeau (*46*) used Raman spectra to identify the products obtained in several reactions while attempting to prepare *p-tert*-butyltoluene and *sym-tert*-butylxylene using alkylation catalysts. He also (*47*) examined the reaction products in the preparation of cyclohexyl-*p*-chlorobenzene by several methods to prove they were the same. Gray (*27*) made a comparative study of the Raman spectra of the different addition complexes of antipyrine and hydroquinone. Kojima (*34*) used Raman spectra to follow the copolymerization process between methyl methacrylate and acrylonitrile. Shemyakin (*60*) outlined the use of Raman spectra and other optical methods in the analysis and evaluation of dyes and their intermediates.

In the field of natural materials Mertens and Hellinckx (*36*) studied the products of the cleavage reduction of Congo copal and identified many of the hydrocarbons boiling between 30° and 189° C. Pigulevskiĭ and Ryskal'chuk (*49*) identified pinene, *d*-α-carene, and 1-Δ^3-carene in their investigation of the fractions of *Pinus silvestris* turpentine boiling between 157° and 172° C. Harispe-Grandperrin and Harispe (*28*) distilled the essential oil from the flower heads of *Inula crithmoides* and by means of Raman spectra showed it to contain *p*-cymene and *d*-α-phellandrene. Dupont and Yvernaut (*14*) obtained the Raman spectra of the methyl esters of fractions prepared by alcoholysis of butter, castor oil, and poppy oil, and showed from the position of the C═C line that oleic acid has the cis configuration while elaidic acid has the trans configuration. It was found also that the C_6 and C_8 fractions from butter gave Raman lines corresponding to a C≡C bond. Yvernault (*76*), in his study of the esters of butter fat, found the same acetylenic bonds.

Comparatively little work has been done on the application of Raman spectra to inorganic materials. Summaries of the work are given in the previously cited monographs and by Simon (*63, 64*). The theory and applications of the spectra of crystals are given by Born and Bradburn (*4*), Cabannes (*5*), and Taboury (*70*).

One of the principal difficulties in using the Raman spectra of inorganic compounds is the change in the spectra caused by the ionization of the materials in water solution. The extent of this change was used by Redlich and co-workers (*56, 57*) to determine the degree of ionization of nitric and perchloric acids.

Simon (*63*) showed the possibility of analyzing 0.1% pyrophosphoric acid in anhydrous ortho acid and Stamm (*67*) showed how the method could be used for the analysis of sodium nitrato—sodium nitrite solutions in water.

Less than 1% of the Raman work which has appeared in the literature relates to the spectra of materials in the gaseous state and virtually no work has been done using this method for analytical work. The principal difficulty is the long exposure time required to obtain measurable spectra. Nielsen and Ward (*42*) used an arrangement whereby vapor-state spectra were obtained in 12 to 36 hours whereas liquid-state spectra were obtained in 5 to 30 minutes. Kirby-Smith and Bonner (*32*) describe an apparatus for obtaining the spectra in 3 to 6 hours at 2 to 3 atmospheres using a high-intensity light source, a large scattering volume, and a large-aperture spectrographic camera. Because of the long exposures and the insensitivity of the Raman method to the detection and quantitative determination of minor constituents in a mixture of gases, this procedure has found little favor among analysts, and the infrared absorption techniques are used almost exclusively for this.

APPARATUS

In the period shortly before 1939 several European optical manufacturers produced a few Raman spectrographs which are described briefly by Kohlrausch (*33*). The war interrupted the development and production of these units and until very recently Raman equipment has been off the market. Many investigators have assembled their own apparatus and there are a considerable number described in the literature. Most of these are described also in the previously cited monographs. Industry has been hesitant in applying the method because of the lack of commercial equipment, and the time necessary to make analyses. Industrial analysts have resorted to the infrared and ultraviolet absorption techniques because good commercial equipment, designed for rapid analyses, is available. Recently one manufacturer introduced a complete line of instrumentation for recording Raman spectra photographically, and this should make the use of the method somewhat more attractive. Several instrument manufacturers are developing photoelectric recording spectrographs which should place this method on an equal basis with the absorption methods with regard to rapidity of making analyses.

Spectrograph. The choice of spectrographic equipment for Raman work is usually a compromise between one that allows large dispersion and good resolution and one that takes a relatively short time for recording the spectra. Because of the small amount of light available by Raman scattering, the effective aperture should not be greater than f10 and should approach f3 to f6, if possible. Dispersion should be better than 35 Å. per mm. in the spectral region to be used. The length of time for recording spectra is limited by convenience, temperature changes in the optical system, vibration of the spectrograph, and stray light. In all but two of the instances given below, the spectra were recorded photographically.

Glass prism instruments are used almost to the exclusion of grating types because of the higher light intensity available. While some Raman spectra have been recorded in the ultraviolet region which requires the use of quartz optics, this region is not used in analytical work because most of the molecules are either not transparent here or are not stable. Liquid prisms are not recommended because of the large temperature coefficient of refractive index.

Rank, Scott, and Fenske (*53*) used a 3-prism instrument with an f4.5 objective which gave a dispersion of approximately 32 Å. per mm. at 4500 Å. Rosenbaum, Martin, and Lauer (*58*) used a three-prism instrument whose dispersion was about 6 Å. per mm. at 4000 Å. and 20 Å. per mm. at 5000 Å.

Stamm (*67*) describes the construction of an instrument employing an echelette-type grating and an objective of f3.6. The dispersion is 36.97 Å. per mm.

Photographic methods of recording spectra are time-consuming and are always attended by the inherent difficulties of development and photometry. Rank and Wiegand (*54*) developed a direct-recording, semiautomatic, photoelectric, grating spectrograph which was used by Fenske *et al.* (*15*) and which gave reproducible spectrograms in about 30 minutes. A nine-stage photomultiplier and direct current amplifier system were used. Chien and Bender (*6*) used a similar arrangement with a prism instrument.

Light Sources. The intensity of scattered light is proportional to the fourth power of the frequency of the exciting line and hence it is advantageous to use as high a frequency line as possible. Practically, however, the analyst is limited in the frequency because of the necessity of using quartz equipment and to the absorption, fluorescence, or photo-decomposition of the sample. The most common source of light for analytical work is the mercury arc which provides, among others, the 5461, 4358, 4047, and 2537 Å. lines. The use of the 4358 Å. line is general, but is dependent upon the elimination of the 4047 Å. line as a simultaneous source of energy. It has been suggested (*67*) that the 5461 Å. line be used for colored substances that absorb the 4358 Å. line but do not absorb in the 5461 Å. region.

The mercury lamps should be of a reasonably high intensity and yet operate at a sufficiently low pressure to produce a narrow exciting line. In general, there is a broad continuum in mercury arcs caused by the mercury fluorescence excited by the 2537 Å. line, which is strong in the region occupied by the Raman spectrum excited by the 4358 Å. line, and the intensity of this continuum increases with pressure. Commercial double-jacketed mercury arcs operate at a constant intensity but the pressure will be considerably higher than that of a single-jacketed arc. Thus, the single-jacketed arcs will produce sharper lines and a less intense continuum. However, with single-jacketed arcs the intensities are much more susceptible to temperature changes. Rosenbaum *et al.* (*58*) use a type H-11 lamp in which the mercury content is reduced to such an extent that the arcs are operated with the mercury completely vaporized. Consequently, they are not temperature sensitive and can be operated cooler than the commercially available arcs with a consequent reduction of the heavy continuum. Rank and McCartney (*52*) have measured the intensity of the background at 4420 Å. for several lamps. Although these lamps were operated at various currents, the data show that the background intensity is proportional to the mercury pressure and also that the intensity of the 4358 Å. line is dependent on the temperature and pressure conditions at both electrodes.

Filters. In order to isolate a single monochromatic exciting line and remove the continuum in the region of the Raman spectrum, filters usually are placed between the light source and the sample cell. Most commonly they are liquid solutions and although they are quite generally used, comparatively little work has been done to find the best materials and the optimum concentrations. Kohlrausch (*33*) and Goubeau (*23*) list a number of the solutions which may be used and Stamm (*67*) gives extensive transmission data for solutions of sodium nitrite, praseodymium chloride, potassium ferricyanide, cupric nitrate, neodymium chloride, and Rhodamine 5GDN Extra from which appropriate filters for isolating the 4358 and 5461 Å. mercury lines can be selected.

Some work has been done to substitute more stable solid filters for the solutions which are generally used. Crawford and Horwitz (*8*) used a Wratten 2-A gelatin filter wrapped around the Raman tube. Glockler and Haskin (*22*) studied filters by centrifugally casting dyed plastic dopes on the inside of glass or methacrylate tubing of slightly larger diameter than the Raman tube. The authors claim that these filters are more convenient when applied directly to the Raman tube since the number of reflecting surfaces is reduced.

Glass filters have been used but the results are not so satisfactory as liquid filters. Interference filters produced by metal evaporation should be satisfactory but no work on these has appeared in the literature.

Sample Cells. Most investigators have used a modification of the sample tube originally designed by Wood with volumes ranging from 1 to 50 ml. In some cases micro equipment using glass capillaries has been necessary (*23*) so that volumes of 0.02 to 0.05 ml. could be examined but alignment of the tube with respect to the spectrograph becomes critical. Recently Nielsen (*40*) developed the theory of condensing lenses for Raman tubes of small volume in order that the maximum amount of light may enter the spectrograph. This should help in the design of equipment so that small samples can be used.

Modifications in the tube design are principally in the jackets for temperature control and filter solutions and in the windows. Some of these are described by Goubeau (*23*) and Kohlrausch (*33*). Fenske *et al.* (*15*) describe a sample tube with two concentric jackets, one in which a praseodymium filter solution is placed and another through which cooling water can be circulated. Nielsen and Ward (*42*) describe a tube in which liquid and gaseous samples can be heated up to 300° C. and Vodar and co-workers (*72*) describe a low temperature arrangement in which a sample is maintained at $-150°$ C. for 200 hours with a variation of $\pm 0.1°$ during the recording of the spectra. Woodward and Tyrrell (*75*) have devised a cell in which solutions containing hydrogen fluoride can be examined using fluorite as a window. Freed and co-workers (*17*) recommend windows of synthetic saphire (aluminum oxide) for use with hydrogen fluoride.

SAMPLE PREPARATION

Contributing to the background scattering, which is an annoying and often limiting factor in the recording and photometry of Raman spectra, is the fluorescence due to the molecular structure of the sample itself or due to dust, oxidation products, or contamination caused by stopcock lubricants, rubber, material extracted from corks and plastic bottle caps, etc. Treatment of the sample by some chemical or physical method prior to the examination of the spectrum is almost always necessary.

Among the chemical methods, Kohlrausch (*33*) lists shaking of organic sulfur compounds with mercury to remove colored impurities and the treatment of iodides with mercury or freshly reduced copper to remove iodine. Goubeau (*23*) recommends the use of ferrous sulfate to remove peroxides from mixtures of unsaturated hydrocarbons while Gerding and van der Vet (*19*) adsorbed the peroxides on charcoal.

The physical methods of sample treatment are distillation, recrystallization, adsorption, filtration, and sublimation. Where the samples are sufficiently volatile the fluorescent impurities are most easily removed by a simple distillation carried to dryness to avoid any fractionation and collected directly in the Raman tube (*15*). Kohlrausch (*33*) describes several procedures for making the distillations. Stamm (*67*) describes a simple vacuum distillation apparatus. Gerding and Nijveld (*18*) used a distillation flask attached directly to the Raman tube from which they distilled liquid sulfur dioxide. Vacuum distillations and even steam distillations may be necessary where the materials are relatively high boiling or are temperature sensitive.

More stubborn cases of fluorescence may be removed by a treatment before distillation with activated charcoal (*24*), activated alumina (*53*), by distillation over clean metallic sodium (*58*), or by passing the vapor through hot activated silica gel before condensation (*15*).

Kahovec and Wagner (*31*) describe an apparatus for the continuous purification of alkylhalides by distillation and passage over copper while the spectra are being examined.

In the examination of solutions, particularly of inorganic salts, filtrations have been used. Kohlrausch (*33*) describes a procedure wherein a solution is shaken with an adsorbent to decolorize it and then filtered through either paper or sintered glass. In the use of paper, extreme care must be observed to remove all paper particles from the filtrate. Simon and Fehér (*65*) used this procedure in their examination of the salts of the phosphorus acids. Simon and Schulze (*66*) used a glass chamber containing a sintered glass disk attached directly to the Raman tube wherein they twice recrystallized orthophosphoric acid to remove the pyroacid. After the recrystallization the acid was decanted into the sample tube.

Small amounts of materials such as nitrobenzene, hydroquinone, resorcinol, or pyrocatechol (*23*) may be added to quench fluorescence in certain cases.

POLARIZATION MEASUREMENTS

Measurements of depolarization factors have been given in almost all work involving the Raman spectra of pure compounds. The actual determination of these values is tedious and rarely sufficiently accurate for analytical work. Recent improvements in apparatus and technique may make it possible to use these data for more reliably determining materials qualitatively and quantitatively. Crawford and Horwitz (*8*) give an excellent review of the various methods used for determining these data photographically and describe an apparatus with which they can be obtained. Douglas and Rank (*12*) have studied the errors arising in the measurement of the depolarization factor of highly depolarized lines and measured some values on a photoelectric spectrograph. With these improvements better values may be obtained.

QUANTITATIVE ANALYSIS

The intensity of a Raman line attributable to a substance in a mixture is a function of the concentration of that substance and quantitative analyses are possible when the intensity-concentration relationships are known. For mixtures of structurally similar, nonpolar compounds it has been found that the intensity-concentration relationship is almost linear (*15, 26, 53*). For mixtures such as acetic or chloroacetic acids and water (*55, 71*), benzene and dioxane (*68*), and electrolytes in water (*35*) the relationship is not a linear one and the position and width as well as the intensity of the line may vary with the composition. In these cases analyses are considerably more difficult.

The determination of intensities has, for the most part, been by some photographic photometry method and the techniques adopted are similar to those used in emission spectroscopy (*16, 48*). The procedures are usually time-consuming and are always attended by the inaccuracies inherent in the photographic technique. Within the past 3 years the trend has shifted to the use of photoelectric Raman spectrographs, with which the intensities may be recorded directly, since this equipment is capable of greater speed and photometric accuracy.

Stamm (*67*) and Goubeau (*23*) have reviewed critically the various schemes of analysis once the intensities of the lines and the intensity-concentration relationships are known. The method which an analyst must choose depends on the type of samples, the number of components, the equipment at hand, the time available, and the accuracy desired.

Grosse, Rosenbaum, and Jacobson (*26*) used perhaps the simplest method in which the spectra of the unknown and a series of known mixtures having the same components were photographed under similar conditions. The blackness of the lines were compared visually to give the composition of the unknown. Crigler (*9*) compared microphotometer deflections for the spectra of a series of known mixtures with the spectrum of an unknown material. These are both only semiquantitative schemes and the results depend to a large extent on the experimental conditions, length of exposure, steadiness of light source, and uniformity of plate development.

A somewhat more refined method for binary systems used by Stamm (*67*) and Gerding and van der Vet (*19*) uses the ratio of the intensities of two suitable lines, one for each compound in the mixture. These ratios, plotted graphically against concentration for a series of known blends, give a calibration curve from which analyses may be made. Ternary mixtures may be analyzed by additional calibrations (*18, 25*).

Rosenbaum *et al.* (*58*) developed a method whereby a four-component mixture could be analyzed.

Rank, Scott, and Fenske (*53*) attempted to decrease experimental inaccuracies by the use of an internal standard (carbon tetrachloride) in their work on hydrocarbon analyses. They defined a scattering coefficient as the ratio of the intensity of the hydrocarbon line in question to the intensity of a particular line of this internal standard. In this method all intensities can be referred to the same intensity basis. Objections are: (1) the contamination of the sample and pure materials by the standard, and (2) the possible overlapping of the standard lines with those of the sample.

Fenske *et al.* (*15*) recording photoelectrically, referred the intensities of the lines of all pure materials and unknown samples to that of the 459 cm.$^{-1}$ line of carbon tetrachloride. For those cases where the intensity-concentration relationship was linear the analysis was made by a simple proportion between intensities. As many as nine components have been determined in a mixture using their method.

An unfortunate deficiency in Raman analytical work, as in all other empirical methods of analysis, is that intensity measurements depend on certain instrument constants and, accordingly, each spectrograph must be calibrated with a complete set of the known pure materials which will be found in the samples to be analyzed. Rank (*50, 51*) has discussed the chief sources of error in intensity measurements and developed equations to enable polarization corrections to be applied to measurements taken on one instrument so that they can be used on another. Chien and Bender (*6*) suggested intensity corrections for the spectral response of the photocathode when recording spectra photoelectrically.

Limitations. Qualitatively Raman spectra have been used to detect constituents in concentrations as low as 0.1% in exceptionally favorable cases. Generally the minimum detectable concentration is about 1%. Quantitatively, these spectra should not be used for concentrations below about 5% when the material scatters light strongly; when the scattering is weak, the minimum concentration is about 10%.

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Ultraviolet Absorption Spectrophotometry

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THE advent of the Beckman quartz spectrophotometer (*10*) just before the recent war marked a turning point in the analytical applications of ultraviolet absorption spectrophotometry, particularly in this country. Before that time a limited amount of work in this field had been carried out, usually on problems for which an alternative solution was impractical or nonexistent. The conventional technique involved photography of spectra, and an arc between metal electrodes was the most frequently used radiation source. In the late thirties the use of photoelectric radiation detectors and hydrogen arc sources was developed. One of the best researches of that time was the work of Hogness, Zscheile, and Sidwell (*21*), who presented a treatment of the fundamentals of absorption spectrophotometry which is still useful today.

The commercial availability of a compact, convenient, and relatively inexpensive spectrophotometer of adequate resolution and stability has rapidly led to a great increase in the application of ultraviolet absorption spectra to chemical analysis, and this increase is partially reflected in the growing literature on this subject. Few instruments have as dominating a position in their field as does the Beckman quartz spectrophotometer at the present time.

INSTRUMENTAL DEVELOPMENT

There has been a considerable amount of interest in employing the Beckman spectrophotometer in ways for which it presumably was not intended. For example, one development (*13*) led to a recording spectrophotometer with an electron multiplier phototube for scanning the whole spectral range from 200 to 400 mμ in terms of per cent transmittance. This was made possible by automatic change of slit-width and correction for change of sensitivity of the phototube with wave length. Another type of change (*27*) resulted in a modified amplifier containing a high impedance direct current to alternating current converter whose stability made the instrument useful for the analysis of a flowing sample at fixed wave length. Several adaptations of the basic instrument to analysis by means of fluorescence have been described (*9, 16*). One investigator (*28*) has reported the use of a mercury arc line source instead of the more usual hydrogen arcs which emit a continuum. This is possible, of course, only when the mercury lines happen to lie within the absorption bands of the substance under investigation.

Although the Beckman spectrophotometer is widely used, some workers use other types of spectral apparatus. Applications to analysis have recently been reported for a grating spectrograph (*26*), a Bausch & Lomb quartz spectrograph (*8*), and Hilger quartz spectrographs (*18, 23*). One investigation (*11*) was directed at the stabilization of the electronic circuits used in conjunction with a Coleman spectrophotometer in order to detect and measure small changes in the absorption of a sample.

The widespread application of spectrophotometric methods requires a good source of solvent (often a saturated hydrocarbon) without appreciable absorption in the spectral range of interest. A practical investigation (*19*) points out the usefulness of silica gel in removing the last traces of contaminants in otherwise satisfactory solvents. Two papers (*17, 29*) are concerned with the absolute calibration of Beckman spectrophotometers and the comparison of data obtained from these instruments with those obtained from other spectrophotometers. They both indicate that the Beckman spectrophotometer showed up favorably in the comparison. One paper (*15*) deals with the intercomparison of a number of Beckman spectrophotometers and leads to the reasonable conclusion that for most accurate results in quantitative analysis each instrument should be calibrated individually, although fair results can be obtained by using the calibration data obtained from one instrument to carry out analyses with another.

APPLICATIONS

Ultraviolet spectrophotometric methods have proved to be important for biochemists and analytical chemists dealing with animal and vegetable fats and oils, and these methods continue to be widely used. A number of investigators have reported analytical studies on fats, fatty acids, and oils (*4, 6, 7, 8, 24*) and on vitamin A (*20, 23*).

Another broad field of application of ultraviolet spectroscopy is the analysis of hydrocarbons containing aromatic rings or conjugated double bonds in the presence of saturated compounds or mono-olefins. For example, this technique is suitable for the determination of butadiene in mixtures of C_4 hydrocarbons, particularly at low concentrations (*27*). Similarly, it has been used for the determination of cyclopentadiene and methylcyclopentadiene (*25*) and for the analysis of C_8 aromatic mixtures (*18*). A quantitative analysis of ternary mixtures of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene (*12*) has been reported. An ultraviolet method for the determination of benzene and toluene in gasoline (*1*, *2*) has been written by an A.S.T.M. group (Committee D-2, Subcommittee XXV, Section F).

This does not begin to exhaust the possibilities of ultraviolet spectrophotometric methods of analysis. Acetone at low concentrations has been accurately determined (*5*). The analysis of mixtures of phenol and the isomeric cresols has been described (*26*). Mixtures of aniline, *N*-methylaniline, and *N*,*N*-dimethylaniline have been successfully analyzed (*28*). The value of the ultraviolet method in the determination of certain inhibitors in polymers has been demonstrated (*3*).

In order to decide whether ultraviolet spectrophotometry would be useful in a particular analytical problem, it is helpful to have at hand the spectra of the compounds of interest. The appearance in the literature of the ultraviolet absorption spectra of many compounds is obviously very valuable. As an example, one recent paper (*22*) presents the spectra of about a dozen anthracene derivatives. The catalog of ultraviolet spectra issued by American Petroleum Institute Research Project 44 at the National Bureau of Standards (*14*) is particularly useful for hydrocarbon analysis, although the spectra of some nonhydrocarbons are also included.

TERMINOLOGY

For many years it has generally been recognized that the terminology of absorption spectrophotometry is in an unsatisfactory state. Such poor terms as "optical density" (almost invariably abbreviated to density) and "extinction coefficient" (absorption coefficient, absorption index) have become entrenched through use. With a large and increasing number of workers (many of whom are not spectroscopists) using spectrophotometric methods for chemical analysis, the need has become more apparent for a set of terms less confusing than that employed up to now and more consistent with usage in other branches of physics. Several organizations, including the National Bureau of Standards, the American Society for Testing Materials, and the Society for Applied Spectroscopy, have become aware of the need and are considering suggestions for improving the situation.

A set of terms for the quantities involved in Beer's law which has much to commend it has been used in a proposed A.S.T.M. test method (*1*, *2*). The word "absorbance" (symbol *A*) is used for the logarithm of the reciprocal of the transmittance, which has previously been called the optical density. The ratio of the absorbance to the product of concentration and optical path length is called the "absorptivity" (symbol *a*). This quantity is a specific property of a material or substance and the suffix "-ivity" denotes that fact. With these terms and their symbols, Beer's law can be expressed as follows:

$$A = -\log \tau = abc$$

where τ is the transmittance, b is the optical path length, and c is the concentration.

Widespread adoption of these terms would seem to be desirable.

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X-RAY ABSORPTION

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IN THE past, when the analytical chemist has used x-rays, he has taken advantage primarily of their diffraction (*15*) by crystalline substances, or of the emission of characteristic spectra. Within recent years, however, it has become possible for the first time to measure x-ray absorption at once precisely and conveniently. As a consequence, x-ray absorptiometry (*23*) will probably become increasingly important as a method of chemical analysis and of chemical control, for the distinctive characteristics of x-rays lead to results unobtainable with the radiant energy now commonly used for these purposes. Measurements of x-ray absorption will not noticeably alter the sample, and a single measurement can often be made in a matter of seconds once the sample is in the beam.

FUNDAMENTAL INFORMATION

The advantages and limitations of x-ray absorptiometry are in general deducible from the known characteristics of x-rays, for a thorough discussion of which the reader is referred to several excellent books (*5*, *7*, *14*, *27*). An attempt is made here to illustrate these characteristics by comparing the absorption of x-rays by bromine with the absorption of the 2537 Å. resonance line of mercury vapor, which resembles more closely the type of process common in absorptiometry as practiced by analytical chemists today.

The outstanding characteristic of x-rays, from which certain others derive, is their high energy, or small wave length (near 1 Å.). Because of this characteristic, the absorption of x-rays usually involves only electrons near the atomic nucleus. The absorption of ultraviolet, visible, or infrared rays, on the other hand, affects the electrons that determine the chemical properties of the elements. X-ray absorption is thus essentially an atomic process and therefore virtually independent of the chemical or physical state. For purposes of chemical analysis, the statements made below concerning x-ray absorption by bromine remain quantitatively valid so long as the mass of bromine is unchanged—be the bromine solid, liquid, or gaseous, elementary or combined, hot or cold, crystalline or amorphous.

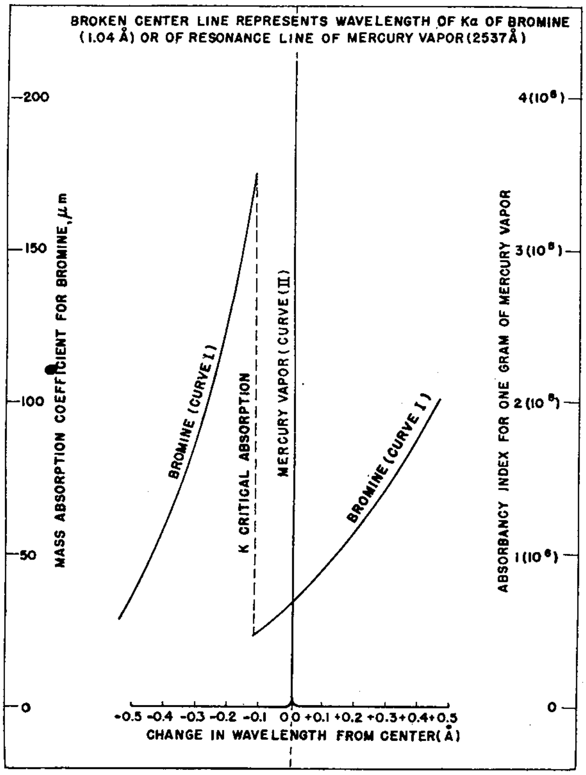


Figure 1. Comparison of X-Rays and Resonance Radiation

In Figure 1, the broken center line represents at once an x-ray (the $K\alpha$ line at 1.04 Å.) emitted by bromine, and an ultraviolet line (2537 Å.) emitted by mercury vapor. The solid curves show how the corresponding absorbancy indexes (*23*) vary in the wave-length region about the emitted line.

The emitted lines are represented identically in Figure 1, but the absorbancy curves differ widely. Curve II, which was calculated from information given by Mitchell and Zemansky (*20*), is symmetrical about the emitted lines and (on Figure 1) indistinguishable from it except near the bottom, where it is approximately 0.04 Å. wide. Elsewhere in Figure 1, curve II coincides with the abscissa. Curve I, on the other hand, is composed of two continuous branches not obviously related to the emitted line and separated from each other by a sharp discontinuity at the "critical absorption wave length" (0.92 Å. in Figure 1).

There are three important differences between curves I and II: (1) Bromine absorbs x-rays appreciably at all the wave lengths shown, whereas mercury vapor is highly transparent over most of Figure 1. (2) For a mass of 1 gram, the maximum absorbancy index is about a million times greater for mercury vapor than for bromine. (3) In the direction of increasing wave length, the discontinuity in the absorbancy curve for mercury vapor is in the direction of increasing absorbancy and coincides in wave length with the emitted line. With bromine, this discontinuity is in the direction of decreasing absorbancy and occurs at a wave length over 10% lower than that of the emitted line.

These differences are readily explained in terms of the atomic processes involved under the simplest conditions. With mercury vapor at low pressures, the absorption of the 2537 Å. line raises one of the outermost electrons in the mercury atom from the ground state to a higher energy level. The emission of this line accompanies the return of this electron to the ground state. With bromine, the absorption of an x-ray in the region below 0.92 Å. ejects one of the innermost, or K, electrons from the atom. The resulting vacancy is then filled by an L electron from the neighboring electron shell, and the characteristic $K\alpha$ bromine line with wave length 1.04 Å. is emitted. The latter wave length thus measures the energy of this electron transfer, which is some 10% less than the energy needed to eject a K electron from the atom. This explains why the critical absorption wave length is less than that of the corresponding emitted line.

The established "absorbancy index" for x-rays is the mass absorption coefficient, μ_m, which is defined by Equation 5. In contrast with absorbancy indexes for the radiant energy commonly used in analytical work, mass absorption coefficients can be expressed as the following approximate function of wave length λ and of atomic number Z:

$$\mu_m = (Z^4 \lambda^3)NC/A \tag{1}$$

where N is Avogadro's number, A is the atomic weight, and C is assumed to be constant in the range between adjacent critical absorption wave lengths. The scattering of x-rays by electrons gives rise to an additive term, usually unimportant except at low Z and λ, that has been omitted from Equation 1.

Because x-ray absorption is an atomic process, the mass absorption coefficient of a sample usually stands in a simple additive relationship to those of the elements present. If, for example, sample S contains elements A, B, and C in the proportions by weight x, y, and $(1-x-y)$, respectively, then

$$\mu_m^S = x\mu_m^A + y\mu_m^B + (1-x-y)\mu_m^C \tag{2}$$

without restiction as to the chemical or physical state of S, A, B, or C. For the purposes of chemical analysis, the mass absorption coefficient of a sample depends only on its ultimate composition and on the wave length of the x-ray beam if the beam is monochromatic. With polychromatic beams, there may occasionally be departures from Equation 2 ("deviations from additivity") which are not discussed in this review (*31*, Figure 4).

TYPES OF X-RAY ABSORPTIOMETRY

X-ray absorptiometry may be subdivided into absorption spectrometry, absorptiometry with filtered beams, and absorptiometry with polychromatic beams, the order being that of decreasing restrictions on wave length. It will not be necessary to discuss the intermediate subdivision, for its usefulness can be estimated from that of the limiting cases for any particular problem.

In absorption spectrometry, the x-ray beam is made monochromatic before it strikes the sample, or the wave-length distribution of the emergent beam is measured by diffraction methods. When this type of absorptiometry is carried out near a critical absorption wave length—e.g., near 0.92 Å. in Figure 1—it can yield both qualitative and quantitative information. When such work is done in regions of continuous absorption, it may usually be considered as a simplified case of absorptiometry with polychromatic beams.

Absorptiometry with a polychromatic x-ray beam somewhat resembles colorimetry with white light. Its most fundamental limitation as an analytical tool is implicit in Equation 1. As all atoms absorb x-rays, such measurements cannot be specific: they cannot ordinarily identify unknown elements in a sample, and (as a corollary) they cannot give the composition of a sample containing unknown elements though they can usually show whether such a sample has an assumed composition or not.

The measurement of x-ray absorption does not differ in principle from similar measurements common in analytical laboratories. For example, polychromatic x-rays from a source (usually a standard x-ray tube) might be passed through the sample contained in a cell, whereupon the emergent beam would enter a detector (photoelectric detector, Geiger counter, ionization chamber) to yield an electric current, i, proportional to the beam intensity, I. When absorption spectrometry is being done, there must be provision for suitably diffracting the beam before it strikes the sample (to render it monochromatic) or after emergence (to analyze it). Neither operation is possible without radically reducing the intensity (say, by several powers of 10) below that of the polychromatic beam.

Under the simplest conditions, the decreases in beam intensity and in output current that measure x-ray absorption by a sample in a cell follow the usual exponential law, which may be written:

$$\log[I_0/I] = \log[i_0/i] = km \tag{3}$$

when I_0 and i_0 refer to the empty cell, k is a proportionality constant that contains the information of chemical interest, and m is the mass of the sample. The effect of certain departures from "simplest conditions" ("deviations from linearity") is discussed below. (For other, less important departures, see the original literature, especially *16, 30, 31.*)

By deviation from linearity is meant a curvature in a plot of i on a logarithmic ordinate against m (or thickness); in other words, a variation in k, the slope of such a plot, and a departure from Equation 3. Such a deviation will occur even with a monochromatic beam if the detection and amplification system becomes nonlinear so that i no longer varies directly as I. One remedy is to restrict the range of operation until satisfactory linearity is achieved. For example, when the range of sample masses is chosen large enough from the viewpoints of convenience and precision, i_0 may equal 1000 i. For samples of masses m_1 and m_2, however, Equation 2 takes the more practical form

$$\log[I_1/I_2] = \log[i_1/i_2] = k[m_2 - m_1] \tag{4}$$

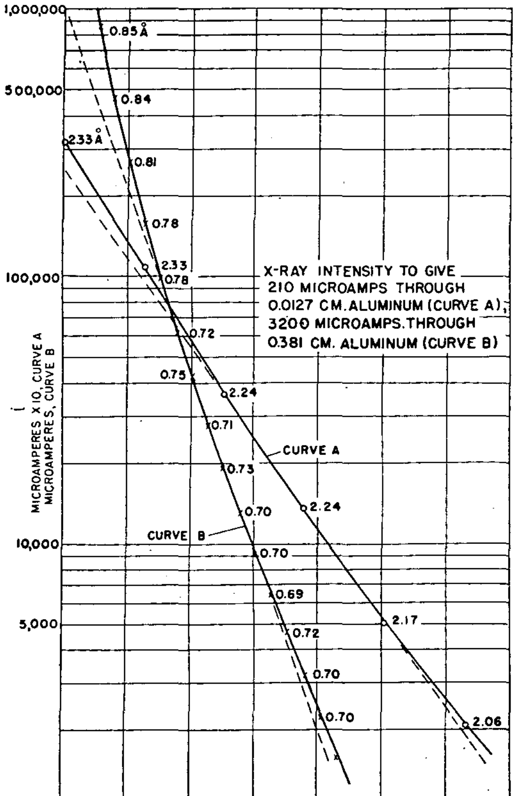


Figure 2. X-Ray Absorbancy Curves for Aluminum over Two Ranges of Thickness

Decrease in effective wave length with increasing thickness of sample is principally responsible for curvature shown, which grows more pronounced as wave length increases.

Another important deviation from linearity peculiar to polychromatic beams is a consequence of the fundamental nature of x-ray absorption. The proportionality constant, k, is related as follows to the mass absorption coefficient of the sample

$$\mu_m = 2.303\,a\,k \tag{5}$$

where a is the cross-sectional area (sq. cm.) of the cell containing the sample. For most elements, μ_m is known to increase approximately with the cube of the wave length (Equation 1) between adjacent critical absorption wave lengths. Consequently, when a polychromatic beam passes through a sample, the longer wave lengths are the more strongly absorbed, so that the beam becomes "harder" as it progresses. It follows that k will decrease as m, the mass of sample, increases. This point is extremely important to the analytical chemist who plans to use polychromatic beams for precise work.

The effect of the deviation just discussed can often be estimated if the change in the "effective wave length" of the polychromatic beam is known. (The effective wave length of a polychromatic beam is defined as that of a monochromatic beam absorbed to the same extent under the experimental conditions.) Figure 2 illustrates the points discussed (*16*, pp. 862–3).

X-RAY ABSORPTION SPECTROMETRY

Absorption measurements near a critical wave length can yield qualitative as well as quantitative information. Glocker and Frohnmayer (*12*), using photographic methods, did the classical work in this field 25 years ago with results that were excellent for the times.

Their method will be illustrated briefly with reference to Figure 1, the assumed problem being to determine the proportion of total bromine (free or combined) x in a sample weighing m grams.

The experimental data will be the results of absorbancy measurements at wave lengths just above and just below (λ and λ', respectively) the critical absorption wave length, 0.92 (more precisely, 0.918) Å. On the basis of Equations 2, 3, and 5,

$$\log I_0/I = k_{\mathrm{Br}}mx + k_S m(1 - x) \quad (\lambda > 0.92\ \text{Å}) \tag{6}$$

$$\log I_0'/I' = k_{\mathrm{Br}}'mx + k_S'm(1 - x) \quad (\lambda' < 0.92\ \text{Å}) \tag{7}$$

$$\text{where} \quad k_{\mathrm{Br}}' > k_{\mathrm{Br}} \quad \text{(see Figure 1)} \tag{8}$$

In these equations, S refers to the sample less the bromine, and the I_0's usually apply to the empty cell. Now, the more nearly identical are λ and λ', the more nearly (in the simplest case)

$$I_0 = I_0' \text{ and } k_S = k_S' \tag{9}$$

If Equation 9 is valid, then by substitution and by subtracting Equation 7 from Equation 6, one obtains

$$\log I'/I = (k_{\mathrm{Br}} - k_{\mathrm{Br}}')mx = -cmx \tag{10}$$

The constant c, which is characteristic for each element and for each absorption discontinuity, can be determined empirically or calculated from known mass absorption coefficients by Equation 5. When either part of Equation 9 does not hold, the effect is to introduce into Equation 10 factors that can be determined by making additional measurements.

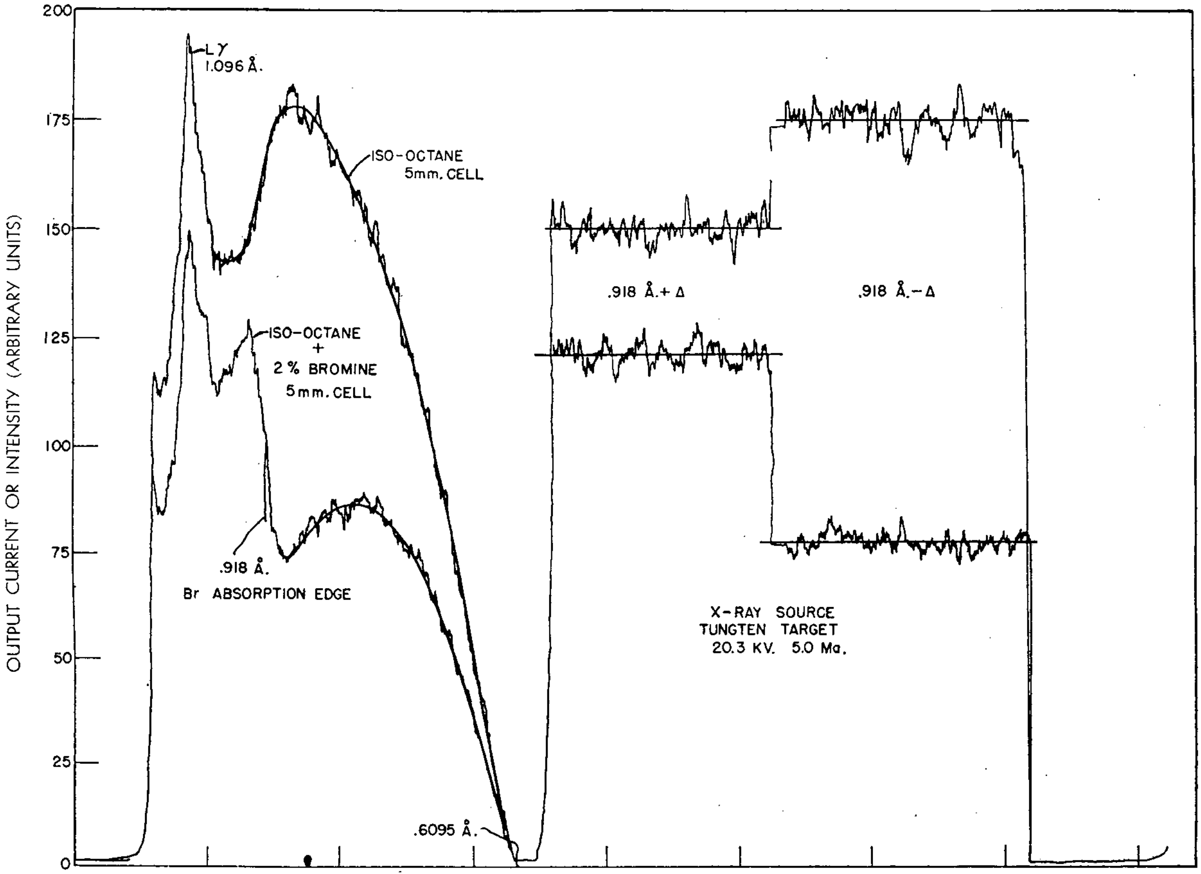
Glocker and Frohnmayer determined the characteristic constant c for nine elements (*12*, Table 4) ranging in atomic numbers from 42 (molybdenum) to 90 (thorium). They proved that identical results could be obtained with the sample in the primary (polychromatic) or in the diffracted (monochromatic) beam. The method was applied with good results to the determination of barium in glass; of antimony in a silicate; of hafnium in the mineral alvite; and of molybdenum, antimony, barium, and lanthanum in a solution of their salts—for example, 5.45% barium was found on 90-minute exposure by the x-ray method for a glass that yielded 5.8% on being analyzed chemically.

Andrews (*2*) used an ionization chamber as detector to determine iron (0.44%) in beryllium according to a procedure resembling that just described. Engström succeeded in applying the method to microscopic sections of tissue and claimed that "in analyses of calcium and phosphorus in biological material, quantities of 10^{-10} to 10^{-11} gram have been determined by the method with an error of 10%" (*8*).

Limitations. The element to be determined may be present in an amount so small that the absorbancy of the rest of the sample near the critical wave length is great enough to make the method insensitive (see Equations 6, 7, and 10), or the characteristic constant *c* may be so small that the precision desired is unattainable. Measurements at certain critical absorption wave lengths—e.g., the *K* series for the light elements—are difficult to make. There may be interference owing to the nearness of critical wave lengths characteristic of other elements in the sample—e.g., the *K* wave lengths of lead and thallium differ by only 0.004 Å. The seriousness of these limitations can sometimes be reduced by selecting a more favorable critical absorption wave length. More important, however, is the promise of progress in this direction that is held out by recent improvements in the equipment available for such work.

Dow Spectrometer. An outstanding example of such equipment is the Dow automatic x-ray absorption spectrometer being developed by Frevel and North (*3, 9, 10, 13*), who are now preparing to publish an account of their work. A cone of polychromatic x-rays passes through the sample and strikes a multiple-crystal "lens" comprising four sodium chloride crystals, the monochromatic beams from which are focused on a Geiger counter so that the sum of their intensities can be automatically recorded as an output current. Variation of wave length is accomplished by having a lathe lead screw move the lens and the detector (at twice the lens speed) along the optical axis. "Voltage is stable to within 0.05% during measurement. . . The probable error of the mean of a single intensity measurement is 0.5% for all measurements made for a period of approximately 5 minutes at rates of 10,000 counts per minute and higher. Repeated measurements give agreement within 1%. The time for an I/I_0 measurement is 10 to 15 minutes" (*9*). After the values of $\ln I/I_0$ measured above and below the absorption edge have been extrapolated to the corresponding critical wave length, the results may be calculated according to Equation 10.

Figure 3 shows the output current records obtained on the Dow instrument for iso-octane and for a solution of ethyl bromide in that solvent. In other words, these may be considered experimental data for the problem assumed near the beginning of this section. As regards precision, time required, and range of determinable elements (now down to atomic number 22), Frevel



COURTESY DOW CHEMICAL COMPANY

Figure 3. Geiger-Counter Output Currents Recorded by Dow Automatic X-Ray Absorption Spectrometer

"Superposed records on left are x-ray absorptiometric curves for iso-octane and a solution containing ethylene dibromide, whereas traces at right illustrate recording of transmitted intensities at fixed wave lengths. Apparent change in x-ray absorption of solvent in going through bromine absorption edge is result of marked slope of white radiation distribution curve at 0.9 Å." (*10*).

and North have improved the method of Glocker and Frohnmayer to the point where it deserves serious consideration by analytical chemists.

Analyses for the lighter elements can of course be carried out on the Dow instrument by making measurements at various wave lengths in the region of continuous absorption; this is the other type of spectrometric method mentioned above. The early work of Wingårdh (*29*) forms a basis for assessing what might be done by this method with modern equipment.

The improved diffraction equipment (*15*) currently becoming available—e.g., Norelco and G.E. XRD-3—can be used, not only for emission spectrometry, but for x-ray absorptiometry of all kinds as well. As this fact becomes more generally appreciated, the importance of x-ray absorption in analytical chemistry will grow.

X-RAY ABSORPTIOMETRY WITH POLYCHROMATIC BEAMS

The use of monochromatic x-ray beams is desirable in chemical analysis because it simplifies the interpretation of results, but there are many applications in which the concomitant reduction in beam intensity cannot (or need not) be tolerated. In general, owing to their higher intensities, polychromatic beams can be used with simpler apparatus. In particular, absorptiometry with polychromatic beams has been made simple and easy by the invention of the multiplier phototube (*25, 32*), which can be readily converted into a photoelectric x-ray detector by the use of a suitable phosphor (see Figure 4). Morgan (*21*), who had been investigating photoelectric cells for the control of roentgenographic exposures, was the first to discover the usefulness of the multiplier phototube in the detection of x-rays. Independently and somewhat later, Smith (*26*) and Moriarty (*22*) made the same discovery in successfully completing a war assignment not fundamentally different from many problems in chemical control.

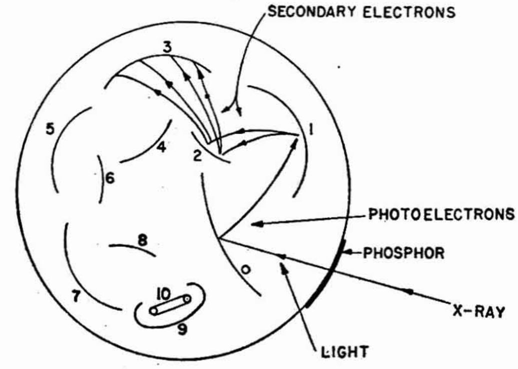


Figure 4. Schematic Diagram of Simple Photoelectric X-Ray Detector

Phosphor converts x-rays into light that liberates electrons from photocathode 0. These are guided electrically to the successive dynodes 1 to 9, where multiplication to give secondary electrons occurs. The greatly (10^5 to 10^6 times) amplified beam is finally gathered by anode 10 for subsequent external amplification (over 10^4 times in photometer of Figure 6), if desired

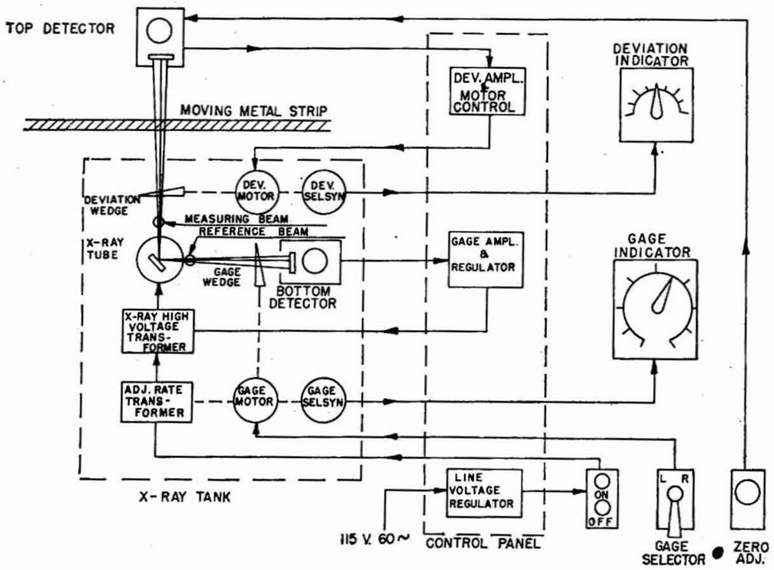


Figure 5. Block Diagram of General Electric X-Ray Thickness Gage

Fuse Testing. This assignment was the devising of an infallible, nondestructive, rapid method of inspecting hand-grenade fuses (*22, 26*). If a fuse contains too little powder, the hand grenade explodes prematurely.

Fuses to be tested were mounted upright on a belt that carried them through an x-ray beam. The absorbance of a fuse containing the proper amount of powder was great enough so that the intensity of the transmitted beam, as measured by a multiplier phototube, was too low to trip the detector circuit. With a defective fuse in the beam, however, the increased output current from the tube set into operation four means of identifying the defective fuse. The equipment inspected fuses at a rate near 4000 an hour, and this rate was not limited by the detecting or recording apparatus.

Thickness of Steel Strip. Clapp and Pohl (*4*) solved another important control problem by using a polychromatic x-ray beam to measure the thickness of steel strip. During the measurement, the strip is hot (1400° to 1700° F.), moving (say, 2000 feet per minute horizontally with possible vertical vibrations up to several inches in amplitude), and subjected to a spray of cooling water.

As is being done to an increasing extent in instrumental analysis, the measurement is accomplished by means of a servo system, whose main features are indicated in Figure 5.

The top and the bottom x-ray detector each contains a multiplier phototube coated with phosphor. This tube compares the intensity of the x-ray beam entering the detector with that of the light from the reference standard, a discharge lamp. The reference beam is part of a circuit that maintains the x-ray source at constant intensity. The deviation wedge comes to rest when the intensities of the transmitted x-ray beams stand in a predetermined ratio. At this point, the unbalance in the servo system has been compensated, and the position of the deviation wedge consequently indicates the thickness of the strip.

It seems reasonable to hope that x-ray absorptiometry with polychromatic beams can be used to solve various other production problems, such as assessing roughly the quality of crushed minerals on a conveyer belt, or controlling the addition of a material—e.g., tetraethyllead to gasoline—to a moving "base stock."

Chemical Analysis. The use of polychromatic x-ray beams in chemical analysis is not new. Fuller (*11*) used photographic means to compare the absorbance of alloys for the purpose of establishing their composition. Aborn and Brown (*1*), acting upon a suggestion of George Calingaert, applied absorptiometry of this type to the determination of tetraethyllead in gasoline and used an ionization chamber as detector. Recently, Sullivan and Friedman (*28*) employed a Geiger counter for the same purpose.

The successful solution of the fuse-testing problem led to an investigation of the photoelectric x-ray detector as a tool for chemical analysis (*17*). The laboratory photometer incorporating this detector is shown in Figure 6. Early work on solids, liquids, and gases was done by the direct method (*16*). The intensity of the x-ray beam was adjusted to a standard initial value by varying the x-ray tube voltage until the desired output current was obtained with a standard thickness of aluminum in the beam, the voltage across the detector and the amplifier setting being fixed. Output currents obtained with known weights of sample in the beam were then used to give information about the composition of the sample. In general, these output currents are plotted as in Figure 2, and the slopes of the curves (or straight lines, Equation 4) are interpreted according to Equations 5 and 2.

To illustrate such an interpretation, a common analytical problem—the determination of chlorine in a chlorinated hydrocarbon polymer—will be briefly discussed (*16*).

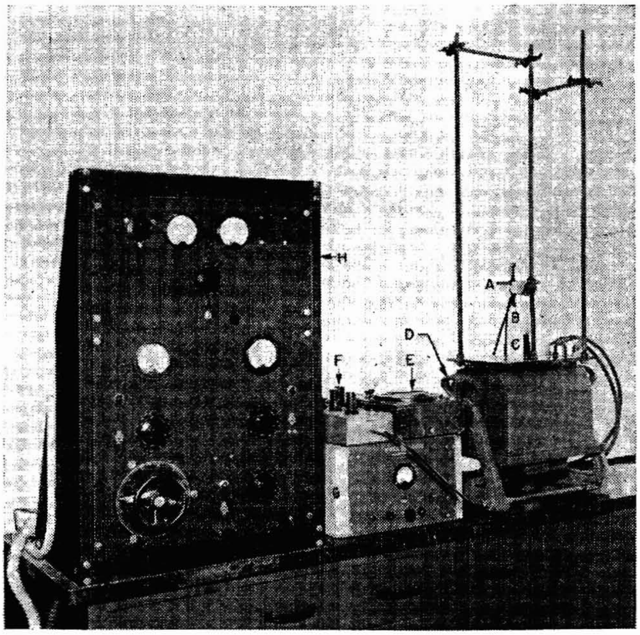


Figure 6. X-Ray Absorption Apparatus

A. Phosphor and multiplier phototube. *B.* Sample cell. *C.* Sample. *D.* (CA-5) x-ray tube and housing. *E.* Milliammeter. *F.* Amplifier and rectifier vacuum tubes. *G.* Regulated power supply for amplifier tubes and phototube anode voltage. *H.* Control panel

Figure 7 contains the k values derived from output current readings for a family of these polymers; the abscissas are the corresponding results of conventional chlorine determinations. The slope-intercept relationship is to be expected in a plot of this kind either when one element replaces another—e.g., chlorine replacing hydrogen—or when an additive is being blended with a base stock—e.g., tetraethyllead added to gasoline. As x-ray and conventional results are in satisfactory agreement (solid line in Figure 7), it is obvious that these data could be used as an empirical calibration curve, with the help of which chlorine determinations could be carried out on unknowns of this type about as satisfactorily as by the conventional method, and in one tenth the time.

So long as the average molecular weight of the polymer is high enough to make end-group effects negligible, the general formula $CH_{2-x}Cl_x$ may be used. Let w be the weight of polymer P containing 1 gram of carbon and deduce the relation between per cent chlorine and the x-ray absorbancy. (Superscripts identify mass absorption coefficients.)

Now

$$w = 1 + (2 - x)\ 1.008/12.01 + 35.46x/12.01 = 1.168 + 2.869x \qquad (11)$$

$$v = \mu_m^C + \mu_m^H(2 - x)\ (1.008)/12.01 + \mu_m^{Cl}(35.46x)/12.01 = w\mu_m^P \qquad (12)$$

where μ_m^P is the mass absorption coefficient of the polymer, and v is defined by Equation 12, which is based on Equation 2. Insertion of numerical values for the mass absorption coefficients of the elements leads eventually to

$$k = 0.082 + 0.01705(\%\ \mathrm{Cl}) \qquad (13)$$

The dotted line in Figure 7 is based on Equation 13. Uncertainties in the mass absorption coefficients of the elements could be wholly responsible for the difference between the two lines in the figure.

The direct method has been used in this laboratory in point-to-point explorations of impregnated materials to test their uniformity. For this work, the diameter of the x-ray beam was reduced (in some cases to 0.15 cm.), and thousands of output-current readings were taken. Each reading gave in a matter of seconds information that would have required several hours to obtain by conventional methods. Moreover, had conventional methods been used, analytical and performance data could not have been obtained on the same specimen, in this case, an overriding consideration.

Though the direct method is well suited to exploratory work and yields results precise enough for many purposes, it is subject to uncertainties arising from voltage fluctuations and from changes in the effective wave length of the polychromatic beam (*31*). For an unfiltered beam of this kind, the variation of output current with primary voltage is much more pronounced than for a monochromatic beam because the change in the total x-ray output affects the current readings in the former case. Rapid commutation in the beam between the unknown and a suitable standard can reduce the uncertainties due to both causes, and the comparative method of x-ray absorptiometry uses this procedure. Readings of output currents are taken alternately for standard and unknown. From these readings, the amount of standard equivalent in absorbancy to the unknown can be calculated. As a consequence, the interpretation of the results does not directly involve output currents, and this is the great advantage of the comparative method. In many cases, aluminum is a satisfactory standard.

The laboratory photometer was used in carrying out the following three types of determinations by the comparative method (*31*): identifications of certain new compounds, determination of tetraethyllead fluid in gasoline, and determination of sulfur in

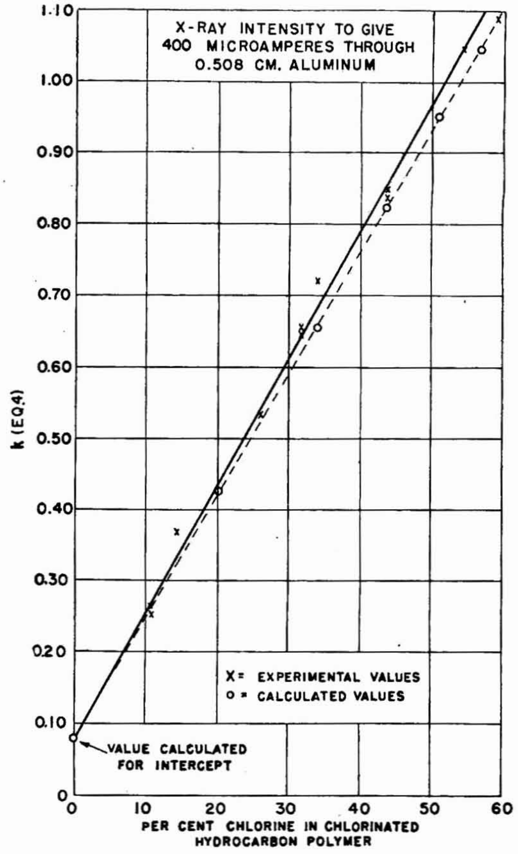


Figure 7. Chlorine Contents of Chlorinated Hydrocarbon Polymers

Absorptiometric results compared with those from conventional analyses

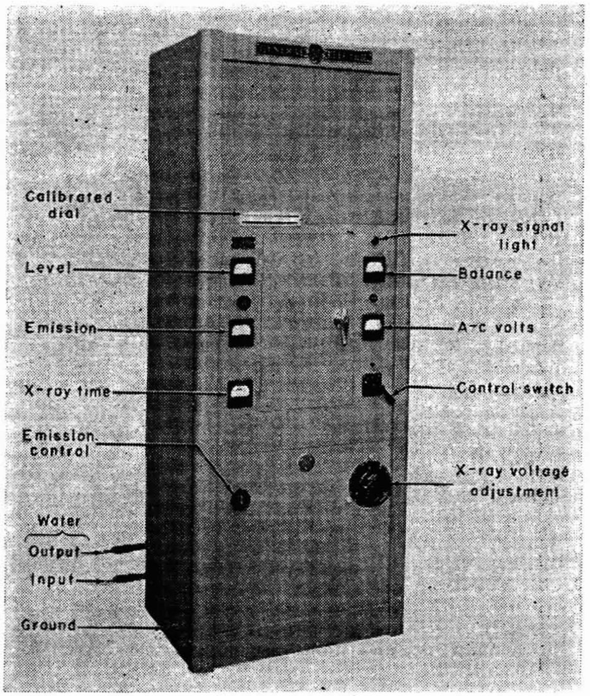


Figure 8. X-Ray Photometer

Front view oblique from left, with parts named

crude oil. The results were generally satisfactory, and the expected improvement over the direct method was realized.

The first type of determination is perhaps the most interesting because it best illustrates the advantages and limitations of the method. Among the advantages is the important fact that standard and unknown need not be the same substance; they need only be the same in ultimate composition. Among the limitations is the fact that a composition for the sample must be assumed so that a standard of this ultimate composition can be prepared. The comparative method can then establish to a high degree of probability whether or not the sample has the composition assumed. The new compounds identified in this way could have contained at most the following elements: carbon, hydrogen, fluorine, and chlorine. The presumed composition of each compound, known in advance, was duplicated by properly blending carbon tetrachloride, benzotrifluoride, heptane, and benzene, and the latter also was used as solvent for the unknown. In four cases out of five, it was concluded that the compounds had the presumed composition and were of good purity; in the fifth, it was discovered on subsequent analysis that excess chlorine was present.

X-Ray Photometer. Because the General Electric x-ray photometer (Figure 8), which was developed by Michel and Rich, uses the comparative method, it avoids uncertainties due both to voltage fluctuation and to changes in the effective wave length (*19*). In fact, the rate of synchronous commutation between standard and sample is so high (30 times per second) that the ordinary 110-volt alternating current usually requires no regulation to be satisfactory as a power source. (Contrast this with the laboratory photometer, Figure 6, for which voltage constancy to within 0.01% is desirable.)

In the commercial instrument, sample and standard are exposed alternately to half of a single x-ray beam, the transmitted portion of which strikes a phosphor to give light collected by a multiplier phototube. When standard and sample differ in absorbancy, the residual unbalance resulting is compensated manually by changing the position of an aluminum wedge. The position of this wedge at balance then measures the absorbancy of the sample, much as the measuring wedge in Figure 5 gives the thickness of the steel strip. To make the operation completely automatic, the photometer can be used in conjunction with a self-balancing recorder. This combination will deliver sufficient power to control the composition of the sample—e.g., to operate a proportioner that regulates the addition of a material to a moving base stock.

So far, the General Electric x-ray photometer appears not to have been used commercially as an automatic controller. It has proved successful on various problems in chemical analysis, and there is reason to hope that data to show this will be published, perhaps in 1949.

CHOICE OF DETECTORS

Whether ionization chamber, Geiger counter, or multiplier phototube (combined with a phosphor) is to be preferred as an x-ray detector is a complex and controversial question, which the analytical chemist is not called upon to answer. He can proceed on the basis that at least one of these detectors is capable of meeting any reasonable requirements he is likely to impose. The ionization chamber, the oldest of the three, has found little or no recent application in chemical analysis.

At the present time, Geiger counters are favored as detectors in x-ray spectrometry although the photoelectric detectors may eventually enter this field in a form resembling Figure 1 (*6*). The low intensity of the monochromatic x-ray beams presents no serious problem for the Geiger counters, and they have been used for measuring such intensities to within 0.01% by means of a comparison method (*24*).

Photoelectric detectors based on multiplier phototubes have commonly served only as instantaneous indicators of x-ray intensity. Because they respond so rapidly (say, 10^{-8} second for the tube and 10^{-5} second for the phosphor) (*18*), they are particularly suited to control applications and to the point-to-point exploration of materials, as in the problem described above. They are more suitable than Geiger counters for realizing the advantages of the comparative method by means of synchronous commutation between sample and standard. In simple direct current applications, they can yield intensity measurements consistently accurate to within 0.1% (*18*); in this laboratory, such accuracy has been approached in some of the analytical work. Careful selection of the tube to be used is advisable. All significant fatigue effects (*18*) have been avoided here, probably owing to the low output current (1 microampere or less) ordinarily drawn. (Small effects of this kind would go unnoticed in the direct method, where the current is initially adjusted to a fixed value with aluminum in the beam, and in the comparative method as well.) The analytical chemist who plans to employ polychromatic beams should seriously consider measuring their intensity with a suitable photoelectric detector.

SUMMARY

Though the unique contribution that x-ray absorptiometry can make to chemical analysis has long been known, attempts to use the technique for this purpose have until recently been sporadic, largely because equipment was not available for making the necessary measurements quickly, precisely, and conveniently. This situation has now changed, and there is reason to hope that measurements of x-ray absorption will assume increasing importance in analytical chemistry. Accordingly, an effort has been made here to give a historical introduction to this field, to describe recent developments in measuring equipment, and to sketch applications of x-ray absorptiometry in chemical analysis and in routine control.

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X-RAY DIFFRACTION

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WITHIN the past 10 or 15 years x-ray diffraction has been established as a most useful tool for analytical purposes. Though not self-sufficient, and incapable by itself of replacing chemical analysis, this method has proved useful for the identification of crystalline substances. Used as a supplementary tool together with other analytical procedures, x-ray diffraction may be relied upon to provide a simple, rapid, and direct method of analysis. There are, in fact, many analytical problems for which only x-ray diffraction can give the required results. This stems from the fact that x-ray diffraction diagrams are characteristic of the compounds rather than of the elements or chemical groups present. Moreover, the amount of specimen required may be very small (about 0.01 mg.) and the experiment is nondestructive.

In this paper the fundamentals of the method are presented together with a review of recent developments in the field in terms of apparatus, techniques, and applications.

A number of books [Barrett (*7*), Buerger (*20*), Bunn (*23*), Clark (*34*), and Zachariasen (*120*)] have adequately treated the theory of x-ray diffraction and, therefore, only a very brief discussion is given here. A crystal is a periodic array in space of its constituent atoms. When monochromatic x-rays are scattered by such an array, interference phenomena occur, and reinforced x-ray beams are observed in specific directions. The angle of scattering, 2θ, of such beams is a simple function of the wave length of the x-rays and of the structure of the crystalline materials. The x-rays can be considered as being reflected by planes of atoms within the crystal. Bragg's law gives this relation:

$$\lambda = 2\,(d/n)\sin$$

where λ is the wave length of the x-ray radiation, θ is the glancing angle and is equal to one half of the angle of scattering, and d/n is the Bragg spacing. For a single crystal the scattering will consist of a few specific beams; for a powder of crystals randomly oriented, the scattered radiation will be localized in the surfaces of right circular cones.

These cones may be recorded on a photographic film where they appear as arcs (in cylindrical section cameras) or as circles (in flat cassette cameras). Instead of film, one may also use an x-ray–sensitive Geiger counter spectrometer with a suitable recording device. This method has proved satisfactory and is finding increased favor among workers in the field.

Because the sizes of atoms and molecules are different, each and every crystalline material has its own set of interplanar spacings. The resulting x-ray diagrams are, therefore, characteristic of the material, since the observed diffraction effects depend upon the interplanar spacings (by Bragg's law).

In addition to the spacings, the intensities of the diffracted lines are also characteristic of the material. Thus the combination of spacings and their associated intensities is sufficient to describe a chemical compound uniquely. X-ray diagrams may, therefore, be used to identify crystalline materials.

In order satisfactorily to utilize the x-ray method for analysis, it is necessary to have an adequate set of standards for comparison. This remains a fundamental limitation to the method, as there are many compounds for which crystallographic data are not as yet available.

POWDER METHOD

The Hull-Debye-Scherrer method of x-ray diffraction analysis is by far the most frequently employed technique for analytical purposes. The details of the method have been described in a number of books (*7, 23, 103*) and papers (*39, 51, 54, 55, 57, 96, 97, 112, 114*).

Hanawalt, Rinn, and Frevel (*57*) described a system for the use of the powder method for chemical analysis. They also made one of the first attempts at systematizing diffraction data by presenting a table of Bragg spacings and relative intensities for 1000 common compounds.

The American Society for Testing materials published a set of index cards containing Hanawalt's list of compounds plus others. A supplement to this set has appeared and a second supplement is in preparation. The present listing contains data for approximately 3000 compounds. The cards contain the d/n spacings of the compounds indexed and cross indexed according to the three most intense lines. The National Bureau of Standards is in the process of preparing a greatly expanded index of crystallographic data.

Various suggestions have been made concerning the best form for the tabulation of the standard reference data. Frevel (*51*) has suggested the grouping of index cards by elements. This is satisfactory if one has preliminary spectrographic or chemical analyses for the elements present.

Bunn (*25*) and Clarke, Kaye, and Parks (*35*) have suggested the use of the innermost line rather than the most intense line for indexing purposes. Matthews and McIntosh (*78*) have reviewed the problem of powder data tabulation and recommend the use of punch cards rather than printed pages, because the former are expandable and provide a mechanical means of sorting. Kronberg (*69*) and Ashley and Newton (*3*) recommend the use of a Kardex (Remington Rand) system for the indexing of diffraction data.

In addition to the above-mentioned A.S.T.M. card index system there are tabulations of minerals (*80*) and ore minerals (*58*). Additional crystallographic information may also be obtained in the *Strukturbericht* (*100*) and Wyckoff's volumes (*117–119*).

A new monthly series giving crystallographic data (*75*) of organic compounds is being presented under the direction of W. C. McCrone. These tables give powder data as well as single crystal data and should provide a very useful set of standards for identification purposes.

APPARATUS AND TECHNIQUES

X-Ray Units and Debye-Scherrer Cameras. There are commercially available at present a number of diffraction units which may be used for analytical purposes.

Baird Associates, University Road, Cambridge 38, Mass., General Electric X-Ray Corp., 4855 West McGeoch Ave., Milwaukee, Wis., Hayes Instrument Co., Urbana, Ill., Adam Hilger, Ltd., London, England (American representative, Jarrell-Ash Co., 165 Newbury St., Boston 16, Mass.), North American Philips Co., 100 East 42nd St., New York 17, N. Y., and Picker X-Ray Corp., 300 Fourth Ave., New York 10, N. Y., manufacture diffraction equipment. These units consist of a suitable power supply and controls, with either sealed off x-ray tubes (General Electric, Machlett Laboratories, Inc., Springdale, Conn., Philips, and Picker) or tubes continuously on the pump (Baird and Hilger).

The powder method of x-ray diffraction actually consists of a number of different techniques, each having its special applications. The most common is the Hull-Debye-Scherrer technique.

This method utilizes a finely ground powder specimen which is rotated in the path of a collimated essentially monochromatic beam of x-rays. The specimen is usually placed on the axis of rotation of a cylindrical camera, but in some cases a flat cassette camera is used. The cameras are fitted with beam traps which prevent blackening of the film at the center due to the primary x-ray beam.

Tubes using a number of target materials are available. Copper target radiation is most commonly employed, because its wave length after being filtered with a thin nickel foil (to remove $K\beta$ radiation) is large enough (1.54 Å.) to give good resolution, and yet short enough to give relatively little air scattering. The short wave length (0.71 Å.) of molybdenum radiation used by Hanawalt and co-workers has a tendency to crowd the lines. A number of elements fluoresce under the influence of copper radiation, resulting in film fogging and background. To avoid this fluorescence other targets must be used. Thus, for work with iron or cobalt samples chromium radiation is recommended. Newly developed tubes utilize beryllium (General Electric and Machlett) and mica (Philips) windows which transmit longer wave length—i.e., chromium—radiation without high absorption.

The diffracted beams are detected and recorded by the use of photographic film, or alternatively by the use of an x-ray–sensitive Geiger counter spectrometer (*40, 53*). The latter method is a recent development in terms of commercially available equipment.

The North American Philips Company (Norelco) introduced the first commercial model in 1945. The General Electric X-Ray Company has announced a spectrometer to be available in the early part of 1949.

The spectrometer units are designed to operate automatically, with the Geiger tube traversing the path of possible reflections. The motion of the tube is coupled to a recording potentiometer. When a diffracted beam enters the tube a peak appears on the moving potentiometer chart. The relative intensities are obtained from the heights of the peaks, while the positions of the lines (in terms of twice the Bragg angle) are read directly from the chart. [A direct reading d/n scale for use with the Norelco spectrometer charts has been described (*50*).] For greater accuracy in measuring intensities provision is made for measuring the counts with a scaling unit. The spectrometer has the advantage of being rapid and automatic while presenting the data in a very convenient form.

For the photographic method of detection one must use a suitable camera. Bradley, Lipson, and Petch (*13*) have discussed the requirements of Debye-Scherrer cameras and described a large (9.5 cm.) radius camera of their design. The larger the camera radius, the greater the dispersion for a given wave length; however, operating against a large radius is the increased time of exposure, so that in design a compromise must be made.

The design of standard diffraction cameras was discussed at a meeting of the English x-ray analysis group (*2*).

Buerger (*19*) has presented a rather complete discussion of powder camera design and describes cameras made according to his specifications. He advocates the use of 57.3- and 114.6-mm. diameter cylindrical cameras. These diameters correspond to factors of 1 mm. per degree and 2 mm. per degree, respectively, in converting from distance on film to angle of arc (θ for use in Bragg's equation). For greater dispersion of lines he recommends a flat film camera at larger distances.

Buerger discusses the motion of the specimen and shows that best results are obtained when the specimen is rotated and simultaneously translated.

The manufacturers of diffraction units supply a large variety, both in size and design, of Debye-Scherrer cameras. In addition, cameras are manufactured by Otto von der Hyde, 78 Winchester St., Newton Highlands 61, Mass., Charles Supper Co., Lincoln, Mass., Unicam Instruments, Ltd., Arbury Road, Cambridge, England, and G. C. Wyland Co., Ramsey, N. J.

For many applications, particularly in the study of inorganics and metals, high temperature cameras are useful. A number of such cameras have been described (*21, 37, 42, 107*). Birks and Friedman (*11*) have described a high temperature attachment for use with the Geiger counter spectrometer.

There have also been described techniques for low temperature work. Lonsdale and Smith (*73*) used a fine stream of liquid oxygen to cool their specimen. Hume-Rothery and Strawbridge (*62*) have designed a camera for controlled low temperature work which utilizes a stream of cold air obtained by evaporating liquid air with an electric immersion heater.

Kaufman and Fankuchen (*66*) have adapted a G.E. 7.20-cm. radius Debye-Scherrer camera for use at low temperature. The specimen is cooled by a stream of nitrogen passed through a copper coil immersed in liquid air. By controlling the rate of gas flow one may control the temperature. The formation of ice is a serious problem in low temperature work and the authors have found that a small double-walled cylinder of thin polystyrene film surrounding the specimen acts as a sufficient insulator to prevent ice formation while the specimen is being cooled by the jet of cold dry nitrogen.

SPECIMEN PREPARATION

The specimens for use with the Debye-Scherrer technique should be very finely powdered (200- to 300-mesh) and may be in one of several forms. Commonly employed for film work are thin-walled (0.01 to 0.03 mm.) glass capillaries about 0.5 mm. in diameter made of Pyrex, or better yet, low absorbing Lindemann (lithium borate) glass. The specimen should not be greater than 0.5 mm. in diameter, since absorption of the x-rays by the sample may drastically reduce the intensity observed on the film. Taylor (*104*) has discussed the optimum thickness of powder specimens. General discussions on the subject of absorption may be found (*20*). If the specimen is highly absorbing it may be mixed with a low absorbing, nondiffracting diluent such as starch or powdered tragacanth (*95*).

Many workers in the field have recommended the use of plastic capillaries. A number of authors (*10, 52, 72, 98, 109*) have suggested that an annealed copper wire be dipped in a solution of plastic and stretched when the plastic is dry. Thin-walled plastic capillaries may then be stripped off. Ness (*89*) has suggested a method of preparing polystyrene capillary tubes by coating thin glass tubes, then cracking or dissolving the glass. Burr (*26*) has used rolled cellophane specimen tubes.

When the absorption of a sample is not known, so that the optimum specimen thickness cannot be determined, one may use the wedge type of specimen. A wedge-shaped sample is prepared using a low absorbing, nondiffracting binder such as shellac. The x-ray beam is directed at the tip of the wedge. This ensures that some portion of the tapered tip will have the optimum thickness. Christ and Champaygne (*32*) have described a cellophane-sealed, wedge-type sample holder for use with materials sensitive to moisture and the atmosphere.

Where a series of reproducible samples is required, the extrusion (*74*) technique may be employed. In this method a die of uniform bore (0.5-mm.) thick-walled capillary tube is packed with the powdered sample which has been mixed with some shellac or collodion. After a short setting period the specimen is extruded with the aid of a wire having the same diameter as the capillary bore.

Barrett and Guy (*8*) have used a special camera for coarse grained specimens which cannot be ground. Switzer and Holmes (*102*) have described an apparatus for obtaining powder type x-ray diagrams from a single crystal, or from coarse crystalline aggregates. This is particularly useful in gem identification.

For lump specimens which cannot be broken and ground; or for the analysis of surface coatings, one may use the glancing angle technique. The x-ray beam strikes the specimen at a small angle and the diffracted beams are thus recorded on only one side of the film, the other side being blocked off by the specimen. Howarth (*60*) and Davison (*41*) have described cameras designed for use with lump specimens.

For metallic specimens which are to be examined in the powder orm one usually uses filings. Hume-Rothery and Raynor (*61*) uggest a method for obtaining uncontaminated representative iling samples.

Marsden (*77*) has described a method for the study of systems ontaining varying amounts of volatile component. This is articularly applicable to hydrates.

ARIATIONS OF DEBYE-SCHERRER TECHNIQUES

A number of specialized variations of the Debye-Scherrer method find wide use for certain applications.

Focusing cameras are cylindrical but unlike the Debye-Scherrer ype are designed so that the defining slits, specimen, and film lie on a circle (on the circumference of the cylinder). The specimen has a large surface and the geometry of the camera is such that the incident beam diverges somewhat, so that a large area of the specimen is irradiated. The diffracted rays reconverge and focus on the circle so that a sharp line is formed on the film. Focusing cameras have the advantage of giving rapid exposures and have twice the dispersion of Debye-Scherrer cameras of similar radius. The latter characteristic is very useful for the study of complex mixtures where the number of lines may be great. Vand (*106*) has described a temperature-controlled Frevel focusing camera. Focusing cameras are available from Wyland, North American Philips Co., Charles Supper Co., and Heyde.

Another type of camera that has special application is the back-reflection camera. This is designed so as to record the diffraction lines at large values of θ. In this region there is high dispersion. These cameras are particularly useful in the study of metals and are available from General Electric X-Ray Co. and Picker X-Ray Corp.

A back-reflection camera designed to permit the study of small spots on metallic surfaces has been described by Wainwright (*108*). Back-reflection focusing cameras have also been described (*7, 27*) and are commercially available (North American Philips, Wyland, Heyde, and Supper).

Many specimens have relatively large d/n spacings (up to 625 Å. for some proteins). For such materials one uses a small angle camera. The specimen-to-film distance is long (from 15 to 50 cm.) and a flat cassette is used. The long specimen-to-film distance permits the measurement of very small values of θ and, therefore, large d/n values.

Chesley (*30*) has described a camera (supplied by Philips) suitable for microtechniques. This is a small scale Debye-Scherrer camera. The defining pinholes are small (down to 25μ). Such a camera permits the examination of very small specimens or small areas on a sample.

MEASUREMENTS OF SPACINGS AND INTENSITIES

The determination of d/n spacings from the x-ray diagrams requires knowledge of the camera radius. This is effectively the film-to-specimen distance. To calibrate a camera one may take a diagram of a standard substance such as rock salt or quartz and use the known spacings to get the radius. An internal standard is frequently used; a known material is mixed with the unknown. This eliminates errors due to film shrinkage or to slight changes in film thickness or position. Wilson and Lipson (*116*) have discussed the calibration of Debye-Scherrer cameras and give precision spacings for quartz. Claassen and Beu (*33*) have suggested a method of applying a correction for nonuniform film shrinkage.

Various short cuts have been suggested for the measurement of x-ray powder diagrams. The straightforward method involves the measurement of the distance between symmetrical pairs of lines. This distance is related to the Bragg angle (θ) by the geometry of the camera. For cylindrical Debye-Scherrer cameras

$$\theta \text{ radians} = s/4r$$

where s = distance between lines; r = radius of camera. For flat cassette cameras

$$2\theta = \tan^{-1} s/2r$$

where r is the specimen-film distance.

The measurement of s is most conveniently accomplished with the aid of a vernier-equipped scale and viewer.

Measuring scales calibrated in 2 sin θ have been described by Fankuchen (*114*). They are independent of wave length but a separate scale is required for each camera radius. One may also construct scales calibrated to read d/n directly. Such a scale is good only for a given radius camera using a selected wave-length x-ray radiation. Scales of this type cannot be expected to give great precision but they are good within 1%, which is satisfactory for most identification purposes.

De Bretteville and Levin (*43*) have described a self-printing interplanar spacing which permits direct measurement of lines in Å.

The International Tables (*65*) list tables of conversion from θ to d/n in Å. for various wave lengths. Brown (*18*) has given a set of conversion tables which also serve to reduce time and effort.

Once the d/n values have been obtained, the corresponding intensities must be determined. These depend upon the atomic distribution within the unit cell. Specimen preparation also affects the intensity. Taylor (*105*) has discussed the effect of heterogeneity on intensity and Brindley (*17*) has discussed the effect of grain size.

Fortunately, relative intensities are generally sufficient, so that most diffraction data are given in terms of I/I_0, where I is the intensity of the measured line relative to I_0, the intensity of the strongest line (taken to be unity).

The unaided eye is capable of detecting very small changes of intensity and visual examination is generally satisfactory. There are also more elaborate methods, designed to give intensity measurements. Robertson (*93*) has presented a survey of the photographic methods of estimating intensity. One of the most useful is the multiple film technique. The known absorption of a sheet of film is used to calculate the relative intensities of lines simultaneously recorded on a set of sandwiched films. Thus the authors have found that Kodak "no screen" double-coated film absorbs 75% of Cu $K\alpha$ radiation.

Brentano has discussed the quantitative evaluation of line intensities (*15*) and has described a microdensitometer (*16*) for use in determining intensities. Ballard, Oshry, and Schrenk (*5*) discuss a number of instruments for intensity measurement, including microphotometers and densitometers.

In addition to photographic techniques, there are the ionization methods and the Geiger counter techniques. The latter are currently being used with great success. New developments have resulted in great sensitivity (at low intensities) and the ability to measure high intensities, plus high resolution. Muehlhause and Friedman (*86*) have described apparatus for very rapid counting (up to 100,000 counts per second) with a Geiger-Müller counter.

The use of the Geiger counter spectrometer has simplified intensity measurements and has provided an excellent method for the application of x-ray diffraction to quantitative analysis.

APPLICATIONS

IDENTIFICATION OF UNKNOWNS

Single-Component. For straightforward identification of pure compounds it is necessary to match the observed d/n spacings and their intensities with the known spacings and intensities of standard materials. This, of course, requires that the crystallographic data be available in one of the published lists, or alternatively that a pattern be available from other sources. Individuals concerned with a particular class of compounds may make up a set of standard diagrams for comparative purposes.

This procedure has been used extensively in mineralogical work. Nagelschmidt (*87*), Peacock (*90*), Bradley (*14*), Harcourt (*58*), and MacEwan (*76*) are among those who have used the x-ray technique for mineral identification.

There are also applications to inorganic chemistry. Weiser, Milligan, and Bates (*113*) have used x-ray diffraction to establish the identical nature of Prussian blue and Turnbull's blue. Birnbaum, Cohen, and Sidhu (*12*) studied samples of ferric oxide of different color and showed them all to be the pure compound of different particle size. Milligan and Focke (*83*) showed the identical nature of aluminum black (formed in vacuum distillation) with pure aluminum. The method has also been applied to identification of organic compounds (*35, 70, 79, 101*).

Multicomponent. More common than single-component unknowns are samples consisting of more than one substance. In such circumstances, the identification procedure is usually more difficult. The diagram consists of two or more intermixed sets of lines. (It is advisable to use a large camera radius or a focusing camera in order to achieve maximum line resolution.) The immediate problem is, therefore, the separation of the lines due to the individual components. Once this has been done each set of lines is treated as a separate unknown.

Frequently the character of the lines from each component differs sufficiently to make separation possible. One set of lines may appear broader or more grainy in appearance. These differences are due to the crystallite size of the components. Very small crystallites give broad lines, while fairly large crystallites give grainy lines even with rotation of the specimen. A method of emphasizing these differences is to take a diagram with a stationary specimen. The different crystallite sizes of the components will then show up markedly and separation may be effected.

Another useful characteristic for line separation is the degree of crystallinity; amorphous and very finely divided materials show very broad halos rather than distinct lines.

There are many applications where the possible components are known and thus the diagrams are simpler to interpret. Milligan and co-workers (*84, 85*) have studied various inorganic systems (including mixed oxides) under differing conditions of preparation and treatment. The x-ray method was used to identify the resulting compounds. Similarly, Erchak, Fankuchen and Ward (*47*) studied the solid phase reactions between ferric oxide and barium carbonate. Milligan (*82*) has reviewed the application of the x-ray method to contact catalysis, including identification of components.

Walton and Walden studied the contamination (*110*) and variable hydration (*111*) of precipitated barium sulfate. X-rays have also been used in the study of phosphors. Nagy and Lui (*88*) observed the chemical changes in phosphors during their preparation and determined proper firing temperatures. Primak, Kaufman, and Ward (*91*) used the back-reflection focusing camera technique to study phosphors by observing changes in lattice constant due to small quantities of foreign material present in solid solution.

The x-ray method has been extremely useful in metallurgical applications (*7, 103*). Lipson (*71*), Edwards (*44*), and Hume-Rothery and Raynor (*61*) have discussed the use of the x-ray method to identify phases in metal and alloy systems.

The x-ray method of identification has many industrial applications in a wide variety of problems. Thus surfaces of oxide-coated cathodes (*45, 46, 49, 96*) have been studied in an attempt to correlate thermionic emission with structure; and crystalline phases of soap (*22, 48*) have been identified by this method. Patterns have been given for the identification of crystalline components of explosives (*99*); and the constitution of "bleaching powder" and setting of plaster of Paris have been studied (*24*). The products of iron corrosion have been investigated by Corey (*38*). Compounds observed in water treatment (*64*), including scale formation (*63*) and corrosion (*81*) have been studied. These are but a few of the many applications that have been recently described.

QUANTITATIVE ANALYSIS

In addition to its use for identification purposes, the x-ray method has been successfully applied to quantitative analysis.

The method is well suited to the determination of percentage composition in a mixed sample and it permits the direct determination of compounds rather than ions or elements.

The basis of the method is that the intensity of diffracted lines produced by a constituent of a mixture is a function of the amount of the constituent present (considering other conditions to be the same). It is, therefore, possible to prepare a set of standards covering any desired range of composition. A comparison of the intensities of lines of the unknown with those of the standards will then give a quantitative determination of the composition of the unknown.

All quantitative procedures require the measurement of intensities of the diffracted lines. This has been done by visual, photometric, or Geiger counter methods. The procedures have been discussed in detail by Ballard and Schrenk (*6*) and Hillman and Jackson (*59*) (photometric method), and by Carl (*28*), Klug, Alexander, and Kummer (*67*, *68*), Redmond (*92*), and Christ, Barnes, and Williams (*31*) (Geiger counter method). Lonsdale (*72*) has criticized some of Carl's assumptions concerning linearity of response of the Geiger counter spectrometer. Carl (*29*) has replied by pointing out that his method yields reproducible results. The introduction of an internal standard (*36*, *56*) has been advocated as a method of correcting for absorption and sample shape and provides a more reproducible method of determining intensities. Alexander and Klug (*1*) have given a mathematical treatment of x-ray absorption as related to quantitative diffraction analysis. An expression for use in quantitative analysis of mixed powders with the Geiger counter spectrometer has been derived by Wilchinsky (*115*). Sampling, mixing, and grinding techniques for quantitative work have been described by Ballard, Oshry, and Schrenk (*4*).

X-ray diffraction methods usually can give analytical results within ±10% of the amount present. In ideal cases results good to ±5% may be obtained. Rooksby (*94*) has shown that amounts as small as 0.11% of calcium oxide in magnesium oxide may be determined.

The x-ray method has been used for the quantitative estimation of minerals (*59*), quartz (*28*, *36*, *67*, *68*) heavy metal carbides (*92*), and organic materials (*31*).

SINGLE-CRYSTAL METHOD

Though not so simple as the powder techniques, the single-crystal method may also be applied to the identification of crystalline compounds. The method is indicated when the specimen is available as a very small single crystal, insufficient in amount for the preparation of a powder specimen. The preparation of some materials in form suitable for the powder method may sometimes produce undesirable chemical and physical changes, and in such cases single-crystal work is recommended. It is also useful for the study of complex mixtures, if a physical separation of single crystals may be effected with the aid of a microscope.

Moreover, many complex systems in which separation is a problem and which, therefore, need physical methods such as x-ray diffraction for analysis are difficult to study with the powder method. Thus the sterols are a group of compounds of similar molecular weights and shapes crystallizing in very similar structures. The powder diagrams of sterols cannot be easily differentiated, but single-crystal x-ray data readily suffice to characterize each sterol (Bernal, Crowfoot, and Fankuchen, *9*).

The single-crystal method has been described in detail by Buerger (*20*) and Bunn (*23*). Among the cameras available for single-crystal work are the Weissenberg camera (available from Heyde and Supper) and the Unicam instrument. These are both designed to give oscillation and rotation diagrams, and the former is also used for moving-film single-crystal methods.

Single-crystal diagrams may give more information than powder diagrams. In addition to a set of *d* spacings, one can obtain the unit cell size rather simply, and from a consideration of the systematic extinctions determine the space group. These data are characteristic of the material studied, and may be used for identification purposes.

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EMISSION SPECTROSCOPY

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IN THIS article attention is directed to the principal postwar spectroscopic advances in fundamental research and applications, in so far as these have been published and are known to the writer. The status of fundamental research in spectroscopy was summarized (*44*) in 1946, and more than 1000 published applications to spectrochemical analysis were indexed and abstracted (*53*) for the years 1940 to 1945 inclusive.

TERM ANALYSIS

Structural analysis and quantum interpretation of atomic emission spectra progressed spectacularly from 1922 to 1940, when World War II interrupted it. Since the war this phase of spectroscopic research is gradually being revived, as evidenced by the following publications.

The $sp^3\ ^5S$ state of carbon atoms was thought to be important for the theory of chemical binding energies of carbon compounds, but its value was unknown until Shenstone (*56*) produced evidence that it is 33,735.2 cm.$^{-1}$ above the ground state $s^2p^2\ ^3P$. The observation of transitions (2965 and 2967 Å.) between these two states implies that ^5S is not a metastable state and should not therefore enter in that role in thermochemical theory. New lines and terms of the first spectrum of fluorine have been reported by Lidén (*40*).

Recent contributions to the analysis of alkali spectra have come from Meissner *et al.*, who employed excited atomic beams and interferometers to resolve some of the ^2D terms of lithium (*48*). A final, practically complete compilation and analysis of the first spectrum of copper has been published by Shenstone (*55*). It appears that the copper spectrum exhibits most of the peculiarities that can be found in atomic spectra. For instance, it has a radically perturbed series, and more examples of auto-ionization than all other known spectra, and is the only example of a complex series converging toward a limit more complex than a doublet. Of its 174 identified energy levels, 110 lie above the level of easiest ionization. The preliminary analysis of the first spectrum of rhenium given by Meggers in 1931 has been extended by Klinkenberg (*38*), who increased the number of classified lines from 500 to 1624.

Spectra of the rare earth type are still the outstanding unfinished business of complex spectrum analysis. The only results for elements containing electrons of 4*f* type, published since the war, are those for Nd I and Nd II by Schuurmans (*51*) and for Yb II by Meggers (*45*). With the aid of the Zeeman effect Kiess *et al.* (*34*) analyzed the first spectrum of uranium. This was the first instance in which the 5*f* electron was positively identified in the ground state of a neutral atom; it appears that the normal electron configuration of uranium is $5f^36d^17s^2$. Similar results for the U I spectrum have been published by Schuurmans *et al.* (*52*), who also reported extensive data for the UII spectrum. Spectroscopic evidence for the electron configurations of elements containing 4*f*- and 5*f*-type electrons was recently summarized (*47*). Progress in the description and analysis of higher stage spectra of light elements was reported by Söderqvist (*59*) for NaIV, NaV, NaVI, MgV, MgVI, and MgVII, and by Ferner (*24*) for AlV to AlXI, SiVI to SiXII, and SVII to SIX.

A large amount of unpublished information on the structure of atomic and ionic spectra will be found in a compilation (*49*) of atomic energy levels which will be issued in several volumes by the National Bureau of Standards. Volume I contains data on ionization potentials, electron configurations, spectral terms, quantum numbers, and magnetic splitting factors (where known) for 205 spectra characteristic of the first 23 atomic numbers, ^{1}H to ^{23}V.

ZEEMAN EFFECT

The most effective aid in the interpretation of spectra is line splitting and polarization in magnetic fields. New observations have been published for NdI, NdII, GdI, and ThII by Klinkenberg (*37*), for SeII, and UI, and UII by van den Bosch (*7*), and for NI and OI by Kiess and Shortley (*35*). Incidentally, the latter are the lightest elements for which magnetic splitting factors have been determined.

ISOTOPE SHIFTS

Measurement of the isotope shift of the red line (6678 Å.) of He^{3} relative to He^{4} was reported (*2*) in agreement with the theoretical value. No satisfactory theory exists for isotope shifts of heavier elements such as have been observed for Nd$^{142,\ 144,\ 146,\ 148,\ 150}$ (*36*), Gd$^{156,\ 158,\ 160}$ (*37*), and U$^{233,\ 235,\ 238}$ (*12*). Irregularities among isotope shifts are a challenge to the theoretical physicist; they must be accounted for by a satisfactory theory of nuclear interactions with optical electrons.

HYPERFINE STRUCTURE

The interaction of optical electrons with atomic nuclei possessing angular momenta results in hyperfine structures of spectral lines, and under favorable circumstances the resolved hyperfine structure yields quantitative results for the mechanical, magnetic, and quadrupole moments of the nuclei. A spin of $9/2\left(\frac{h}{2\pi}\text{ unit}\right)$ for Cb^{93} has been definitely established (*43*). Partial resolution of a hyperfine pattern indicates (*1*) a spin of 5/2 (or possibly 7/2) for U^{235}, and from the fact that lines of Np^{237} exhibit a maximum of six components it is concluded (*62*) that this nucleus has a spin of 5/2. From measurements of alternating intensities in band spectra of carbon compounds, Jenkins (*33*) has shown conclusively that the spin of C^{13} is 1/2 and of C^{14} is 0. If this review were not confined to conventional emission spectroscopy, mention could be made of spectacular and important measurements of nuclear moments by means of magnetic resonance and by microwave techniques derived from the development of radar during World War II. These measurements have been made not only on chemical elements (H, D, T, He, C, N, K, Cl, Br, Cu, Ga, etc.) but also on elementary particles (electron, proton, neutron).

NEW ELEMENTS

Stupendous neutron flux density in chain-reacting uranium piles has resulted in the manufacture, either by transmutation or by fission, of tangible amounts of artificial isotopes or new elements, thus expanding the domain of spectroscopy. Publication of spectroscopic data on these artificial elements is still very meager, but the following may be cited.

The K-x-ray spectra of ^{43}Tc and of ^{61}Pm have been described (*10, 11*). Hg^{198}, produced by transmuting Au^{197}, emits superlatively sharp spectral lines whose wave lengths suggest themselves as the ultimate standard of length (*46*). The spectra of transuranic elements have not been fully revealed (or studied), but for identification one line (4164.5 Å.) characteristic of ^{93}Np and one line (3709.1 Å.) characteristic of ^{94}Pu have been disclosed (*25*). A large program of stable-isotope separations at Oak Ridge has further extended the possibilities of spectroscopic research, especially in the study of isotope shifts and hyperfine structures. In fact, the number of possible and profitable problems in fundamental spectroscopy is at present many times greater than the number of persons actually engaged with them.

SPECTROCHEMICAL ANALYSIS

Whereas practically all postwar published research in fundamental spectroscopy has been cited here, to do likewise for emission spectroscopy applied to spectrochemical analysis would entail a bibliography of more than 400 papers. The majority of these deal with quantitative analysis of metal alloys, in which field spectrography had already displaced classical chemical methods, except for the determination of gases, sulfur, and carbon.

The possibility of determining carbon in steel by a spectrographic method using a simple condensed spark has been investigated by Garton (*26*). Techniques for the spectrographic determination of boron in steel were developed (*18, 41*) as a wartime problem. The colossal size of the metallurgical industry and the necessity of adequate composition control of complex alloys have justified the development of expensive source units and direct-reading spectrometers. The latter eliminate photographic recording, processing, and measuring by employing as detectors electron-multiplier phototubes that charge condensers, which then actuate mechanisms calibrated to indicate per cent composition. Such direct-reading instruments and their use in the spectrochemical analysis of steels have been described in some detail (*15, 30*). Similar applications of direct-reading instruments to analysis of nonferrous alloys have also been made, for example, to magnesium alloys (*50*) and to aluminum alloys (*4*) in which more than 100,000 element analyses per month are possible. Direct reading of 20 elements in light alloys has been described (*6*).

Application of Geiger-Müller counters in the direct determination of phosphorus in steel should also be mentioned (*9, 28*); likewise, spectrochemical analysis with the oscillograph (*19*). Notable progress has been made in the spectrochemical analysis of lubricating oil additives, additive lubricants, and gasolines (*14*), of minor constituents in portland cement (*31*), of rare earth elements (*22, 23*) and of ceramic and other nonmetallic materials (*32, 64*). Two papers on a method of analysis based on photographic line widths (*17, 20*) claim that this method is independent of exposure time, photographic development, and self-reversal, and is, therefore, more precise than the photographic-density method.

The manufacture of atomic bombs was responsible for the development of a carrier-distillation method of analyzing uranium for 33 volatile impurities (*54*), and a copper-spark method of analyzing plutonium for 64 other elements (*25*). That applied spectroscopy can give warning of toxic elements is illustrated in the spectrographic determination of beryllium in biological material and in air (*16*), and in the development of a rapid mobile analyzer for minute amounts of lead in air (*3*). Recent attempts to detect and determine gases spectrographically are solely represented by experiments with halogens excited either by ultra-high-frequency electric fields (*27*) or in hollow cathode discharges (*42*). There appear to be only two recent examples of isotopic analysis by means of atomic spectra; these are the determination of deuterium in hydrogen (*61*) and concentrations of U$^{233,\ 235,\ 238}$ in uranium samples (*12*).

Efforts further to improve the accuracy of spectrochemical determinations have brought forth other modifications of the classical spectroscopic arc and spark sources: a condensed arc source (*57*), a combination arc-spark source (*13*), a combination spark-arc source (*29*), and a general purpose source providing a simple condensed spark, a direct current arc, and intermediates (*63*). The low-voltage controlled alternating current arc is claimed to be an improved source (*8*) and a study concerning characteristics of the high-voltage alternating current arc has been reported (*5*). An air-interrupter type of spark source has also been described (*21*).

Despite a reputation for instability, the direct current arc has not been discarded, and the reasons for its continued use are not far to seek. Compared with elaborate and expensive controlled sparks, high-voltage alternating current arcs, and multisource units, the direct current arc is absurdly simple and cheap; it requires only an electrode holder and a rheostat. Because of a large power consumption and high temperature the direct current arc is most efficient in vaporizing and exciting refractory materials; recent applications to the spectrochemical determination of the major constituents of minerals and rocks (*39*), and to quantitative analysis of ceramic and other nonmetallic samples (*32*) and of rare earth oxides (*22*, *23*) have been reported. Because the direct current arc is the least ionizing of the electrical sources, it favors the excitation of neutral atoms whose strongest lines occur in the observed range of spectrum, and consequently it is naturally superior in detectability of trace elements; for this reason it is necessarily used in the spectrochemical analysis of high-purity materials (*58*).

The main cause of poor reproducibility usually asssociated with the direct current arc source has been traced to fractional distillation. Strock and Heggen (*60*) have shown that reproducibility is greatly improved by employing an internal standard with excitation properties comparable with those of the analysis lines. Fassel (*22*) has obtained high precision by nearly ideal internal-standard compensation of excitation variables; if the internal standard and analysis elements have similar physical properties, the intensity ratios of line pairs are independent of current, weight of charge, per cent of graphite, depth of cavity, length, and region of the analytical gap. Satisfactory precision may be expected from any spectroscopic source, provided the necessary conditions of the internal-standard principle are fulfilled. Perhaps too much emphasis has been placed on electrical apparatus and circuits and not enough on the physical properties of the chemical elements to be detected or determined. Unfortunately, the melting and boiling points of some elements are still unknown or very uncertain. Likewise, the excitation characteristics and relative intensities of many spectral lines are unknown.

In conclusion, attention is called to the present disparity between fundamental and applied spectroscopy—for every research spectroscopist there are now hundreds of spectrographers, and for one paper on fundamental spectroscopy there are at least ten on applications. Publication of an international journal of applied spectroscopy, *Spectrochimica Acta*, founded in 1939 and suspended in 1944, was resumed in 1947, and in this country a half dozen or more societies of applied spectroscopy have been organized, at least one of which is publishing a *Society for Applied Spectroscopy Bulletin*. No one can find fault with this amazing activity in applied spectroscopy, but, remembering that progress rests upon new knowledge, it is extremely important to attract more investigators to fundamental research.

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MASS SPECTROMETRY

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THE statistically inclined might draw inferences from the fact that *Chemical Abstracts* reported 11 references to mass spectrometry in 1943, 15 in 1944, 17 in 1945, 26 in 1946, and 40 in 1947. If the war jam could be properly discounted, an indication of increasing interest would probably remain. Actually, there is no doubt of the sharply increasing interest and importance of the mass spectrometer as an analytical tool. It is capable of resolving rather terrifying mixtures of gases, vapors, and even solids and liquids, within an astonishingly short time, and with reasonable and sometimes superior accuracy. Applications of the instrument are continually increasing, and its use in research and control has expanded beyond general anticipation, not only in the gas, petroleum, and chemical industries, but even in the biological as well as physical-chemical sciences.

A census of the mass spectrometers in use today discloses a curious situation. There are a number of special-purpose instruments, designed for specific masses over narrow ranges. Aside from leak-detecting spectrometers, these are mostly assembled in the laboratories using them. There are a few metallurgical instruments designed for analysis of solids and an increasing number of isotope ratio instruments. But commercial presentation has so far centered on a general-purpose analytical instrument of wide mass range, about 0 to 200, with good resolution somewhat over 100. About 70 of these are operating now, and they are performing a good share of the more accurate gas analysis being done in this country. Of these instruments, about 10% were made by Westinghouse (which no longer manufactures this item) and almost all the others by the Consolidated Engineering Corporation, Pasadena, Calif. (General Electric and a few others are now entering the field.) Consolidated Engineering Corporation maintains research and engineering groups and exchanges technical information between users of the instrument through regular group meetings. Thus the corporation and its customers offer a contribution to this special analytical field that is unique at the moment. The reports of the Consolidated group meetings contain valuable material, all of which has not been published. Occasional reference is made here to these reports, as this information may be made available by the authors.

ANALYTICAL APPLICATIONS

The analytical mass spectrometer is primarily an apparatus for gas analysis and has offered the first actual systematic approach in this field. Within fairly wide limits it is possible to identify and determine the components of simple and complex mixtures of hydrocarbons, fuel gases, exhaust gases, rare gases, and special samples of many kinds.

Instruments, procedures, and typical analyses of mixtures of various kinds have been reported by Washburn, Wiley, Rock, and their associates (*169, 170*), Hipple (*63*), Brewer and Dibeler (*17*), Brewer (*15*), Coggeshall (*26*), Farmer (*44*), and others. Somewhat less general applications have been discussed by Smyth (*144*), Nier (*115*), Hipple (*62*), Rittenberg (*123*), Eltenton (*40*), Watson, Buchanan, and Elder (*171*), Hipple and Condon (*65*), and others. These papers disclose spectrometric analyses of most of the common and rare gases, and of the hydrocarbons through the C_4 group.

More general treatment has been given in papers discussing industrial analysis by the mass spectrometer and comparing results obtained with those yielded by more conventional methods: Solomon and Rubin (*146*), Schaafsma (*128*), Milsom (*104*), Crone (*31*), Fulton and Heigl (*50*), Brewer (*16*), Webb (*172*), and Schlesman and Hochgesang (*132*).

Analyses of specific compounds and mixtures have been reported, but the account is far from complete. Dibeler and Mohler have discussed the analysis of a mixture containing C_3–C_5 paraffins and olefins, with emphasis on sampling difficulties (*38*).

The determination of hydrogen with the mass spectrometer has been thoroughly discussed by Honig of Socony-Vacuum Laboratories (*68*), and new techniques recommended correct what previously was a sometimes unsatisfactory determination. The analysis of hydrogen and hydrocarbons (*79*) and of H_2 and D_2 (*9*) has been reported. The determination of butene isomers in hydrocarbon mixtures has been discussed (*6, 99, 126*). The determination of oxygen (*53*), nitrogen (*61*), and of carbon (*54*) in organic compounds has been described.

Analyses of specific mixtures include rare gases (*39*); and ethylene oxide with ethylene and carbon dioxide, silicanes, aliphatic derivatives, ethers, and other organic mixtures (*153*).

Although the analytical mass spectrometer in general use is a gas analysis apparatus, it is, of course, capable of producing spectrograms representing mixtures of the vapors of various liquids. Heavier vapors, particularly those of polar substances, have caused trouble because of strong sorption; but recently this difficulty has been largely overcome by introducing the vapor sample almost directly into the ionization chamber, or heating the entire inlet system. As a result of these improved techniques, the analysis of water vapor and alcohols up through C_4 has been made possible, and analyses of alcohols, aldehydes, mercaptans, and other liquid organic compounds have been reported (*22, 30, 124, 158, 166*). The analysis of liquid hydrocarbon mixtures in the C_5 to C_8 range is reported by Brown, Taylor, Melpolder, and Young (*20*), who found that paraffins, cycloparaffins, and aromatics may be individually determined, but olefins and cyclo-olefins only to a limited extent. The analysis of mixtures containing pentenes, pentanes, and isoprene (*19*) and of heptane mixtures (*21*) has been reported by Brown. Rock has discussed the analysis of octane mixtures (*125*). Thiophene mixtures have also been analyzed (*145*).

While the mass spectrum of a complex mixture may be obtained in a few minutes, the analysis and computation of the spectrum may require several hours or even longer. Normally three computers per 8-hour shift are required for one spectrometer. Comparatively little has been published, with the exception of the Consolidated Computing Manuals prepared by Rock, a similar manual prepared for the users of Westinghouse instruments, and a series of reports dealing with spectrometric computational methods, probable errors, and reciprocal matrices, prepared by the Texas Company's Technical and Research Division (*154*). Other contributions are: computation of C_1 to C_5 hydrocarbon mixtures containing carbon dioxide by Brown (*18*) and a new method of analysis by Johnsen (*78*).

The catalog of mass spectral data issued by the American Petroleum Institute Research Project 44 and the National Bureau of Standards has been very helpful in the study of spectrograms, particularly so in the identification of substances for which no patterns are otherwise available (*109*).

The accuracy and reproducibility of the mass spectrometric analysis and of the conventional chemical volumetric analysis have been compared by 50 laboratories throughout the country in the cooperative analysis of a standard sample of natural gas (*135*). The mass spectrometer in general gave the better account of this sample from the viewpoints of accuracy and completeness of composition.

In many instances the mass spectral method could be a valuable supplement to the optical spectrograph in the analysis of solids, but there has been little attention to this field. Shaw and Rall

(*134*) have redesigned an instrument of the Mattauch type with this aim in mind. Hickam (*60*) has employed the mass spectrometer for the detection of small impurities in certain metals by completely evaporating the sample and comparing the integrated time-current curves for the various components. Grosse (*53*) has made a limited application of the conventional instrument for gas analysis to this purpose. Extremely high sensitivity has been achieved, but reproducibility has not always been satisfactory.

INSTRUMENTATION

There has been no major change in recent years in the type of instrument in general use for gas analysis—an ion source providing a monoenergetic beam that is analyzed by a magnetic field. However, refinements have been made as the result of broadened experience gained in the vigorous extension to practical analytical problems. These refinements have permitted an increase in the accuracy and speed of individual analyses, resulted in somewhat simplified operation, or extended the range of problems that may be handled by this general technique. In most cases there is no published reference for these improvements which have rather naturally evolved since the time, approximately 5 years ago, when suitable instruments became more generally available. Descriptions of instruments that have been custom-built in various laboratories (*5, 51, 67, 85, 91, 107, 152*) offer some individual variations of special interest to the particular designer. Nier (*113*) has continued his role as instrument designer for those nonspecialists who desire to use instruments incorporating the latest developments by publishing very detailed design information, a sequel to his earlier paper on this subject.

In the field of isotopic measurements the greatest single advance (*112*) has been the development of a null method for the comparison of two ion currents (*116*). The output of a feedback amplifier on the more abundant ion is used to balance out the simultaneously measured signal of the less abundant ion, so that the ratio of the two currents is continuously measured.

In order to reduce the mass discrimination (*27*) and widen the mass range that may conveniently be scanned without discontinuity, the trend has been toward magnetic rather than electric scanning (*67, 74*).

The four-element oscillograph (*169*) has been the most widely used recording method. The range limitation of the single element pen-and-ink recorder has been circumvented by the use of an automatic scale expander (*55*) with some modifications (*37, 92*).

For continuous visual observation of the mass spectrum the cathode ray oscilloscope has been used. Forrester and Whalley (*46*) have used a long persistence screen with a sweep of frequency as low as 1/30 cycle per second to obtain a sensitivity comparable with instruments with conventional recorders. Siri (*140*) employed a sweep frequency of 200 cp. and his pattern indicated a resolution of mass unit in 65. These devices find application where the merits of this type of observation permit the sacrifice of accuracy.

One of the ever-present limitations on the extension of the range of the existing instruments is the first amplifying stage for the ion current. Consequently, new methods of detection or improvements in old ones are of immediate interest. One development that has been announced since the end of the war is the capacitative commutator or dynamic condenser electrometer (*119, 120, 130, 131*). This has extremely low drift, low background current, and high sensitivity. One of the chief objections to this system at present is its high initial cost. The stability and ease of balancing the electrometer tube circuit have been improved with the advent of the split-beam electrometer tube (*86*). New circuits (*23, 111*) have improved the performance with the tubes that have generally been used in the past. Millest (*102*) has concluded that the space charge detector is less sensitive than the electrometer for detecting small currents of positive ions. The use of Be-Cu, which has been found to be very stable in electron multipliers (*4*), makes this very attractive for use where extremely high sensitivity is required or the speed of response would otherwise be limited by the time-constant of the input circuit of the electrometer tube.

More careful attention to the ion optics of the source has resulted in greater resolution in peaks varying widely in intensity. The "tails" at the bottom of large peaks have been reduced by the use of an energy filter between the exit slit and the ion collector to reject those ions which have been scattered in the analyzer with an accompanying loss of energy. This has been done by the addition of a suppressor electrode to which a high retarding voltage is applied (*118*) or simply by operating with the ion source near ground and the analyzer at a high negative potential (*47*).

A recording mass spectrometer for process analysis has recently been described (*114*). Instruments for the continuous analysis of respiratory gases are under development (*35*). Several review articles have appeared in the past few years (*1, 34, 97, 155*).

The use of a mass spectrometer of simplified design for leak detection was described in the Smyth report (*144*). There has been an expanding interest in this application since the war because of its widespread usefulness (*76, 118, 159, 160*).

New methods of mass analysis have been considered in the design of other instruments. Several time-of-flight mass spectrometers have been proposed (*11, 24, 147, 173*) and two have recently been built (*11, 24*). In the one type (*24*) a pulse of ions is sent down a drift tube and the arrival time depends on the mass with the spectrum displayed on a cathode ray screen. In the other type (*11*) the ions are accelerated through a series of grids on which rf potentials are applied. For a particular geometry and frequency, the phase will be appropriate for ions of one mass as they pass through the grids to receive more energy than others and hence these can overcome a stopping potential at the end of the tube and reach the collector. At the present stage it appears unlikely that these methods will supplant the conventional ones in the near future for accurate isotopic and gas analysis, as the requirements of the source, of the amplifier, or of both together are not eased (and in most respects they are made much more severe); the elimination of the magnet is of minor importance when precision of analysis is being stressed. Their possible use under less stringent circumstances warrants a continued exploration of their possibilities.

Goudsmit (*52*) has described an arrangement in which a pulse of ions describes a helical path in a uniform magnetic field. As the time for rotation through 360° depends only on M/e and the value of the magnetic field rather than the initial conditions, he proposes to make a precise comparison of masses by timing the arrival of ions of different types at the collector after rotation through 2π.

Studies have continued on the focusing properties of static electric and magnetic fields. These have had for their purpose the increase of intensity and resolution by the use of nonuniform fields of such form that higher than first-order focusing is obtained or to provide for axial focusing in the direction of the main component of the magnetic field (*10, 13, 28, 29, 87, 137–139, 150*). The focusing of a uniform magnetic field superposed on a crossed electric field from a cylindrical condenser has recently been investigated for relativistic energies (*103*). The effect of the fringing magnetic field and the angle of entry of the beam into the sectored magnetic field analyzer has been studied theoretically (*80, 88, 96*). Bainbridge (*8*) has given formulas for the proper shapes of the edges of the pole faces, in order that second order focusing may be obtained. Koch (*82, 83*) has eliminated the necessity of a high degree of stability on the ion accelerating voltage by employing compensating electrostatic deflectors in the magnetic analyzer. Nier, Roberts, and Franklin (*117*) describe a double focusing mass spectrometer in which second-order focusing is obtained; stability of 1 part in 10^6 is attained by controlling the ion beam by the signal from an auxiliary monitoring beam.

The theoretical treatment customarily used in electron-optical devices has been applied to the mass spectrograph by Hutter (*72*).

ISOTOPES

Abundance. The unspectacular but very important measurements of the natural abundance of the stable isotopes have continued (*3, 8, 59, 73, 98, 157, 175, 176*). Aldrich and Nier (*2*) have been able to make the very difficult measurement of the He^4/He^3 ratio with the He^3 peak completely resolved from the impurity HD and thus showed the large difference between atmospheric helium and well helium. This development is of particular importance in providing a means of testing the various methods for concentrating He^3. Urey (*162*) has recently extended the accuracy of comparing the isotopic abundances of different samples by using the balanced beam method (*116*) in conjunction with an arrangement for inserting a control sample every 2 minutes. A recent monograph describes the preparation and measurement of isotopic tracers (*121*).

Mass. The accurate measurement of masses received practically no attention during the war, but it is a field in which much work remains to be done and attention is being directed to it (*33, 42, 43, 80, 122*). A critical review of the existing data has recently been made by Bainbridge (*7*). Although the photographic method has been used almost exclusively, the use of electrical detection is now being seriously attempted (*110, 117, 125*).

Concentration of Isotopes by Mass Spectrograph. The large scale concentration of U^{235} has been described in the Smyth report (*144*). A more detailed description of separation in quantity by electromagnetic means has been given by Smith, Parkins, and Forrester (*143*). Because this is the only source of many of the separated isotopes, continued interest in this field is assured (*25, 81, 84, 108, 151, 164, 165*).

Identification and Mass Assignment of Products of Nuclear Reactions. There have been many letters, abstracts, and papers on this subject principally by the Chicago group—A. J. Dempster, M. G. Inghram, R. J. Hayden, D. C. Lewis, Jr., A. E. Shaw, W. Rall, and others. Bainbridge has reviewed this work up to August 1947 (*7*). In the autoradiographic technique, the mass spectrum of an element is obtained in the usual manner and the radioactive isotopes are then identified by laying an unexposed photographic plate against the exposed one—only the radioactive isotopes will give lines on the second plate. In some cases a counter is used instead of the second photographic plate (*58, 90*). The mass spectroscopic method in many cases offers the only clear-cut identification of the stable or very long-lived products of nuclear reactions (*14, 32, 75, 133, 156*).

STUDY OF IONIZATION PROCESSES

Applications to Chemistry. As the study of ionization processes with the mass spectrometer was the forerunner of the application to routine analysis, it is clear that these more fundamental studies will be of continuing interest to all workers in applied mass spectroscopy. Measurements have continued on the appearance potentials of the various fragment ions, the study of secondary processes of ion production, and the compilation of data on the mass spectra of additional substances (*12, 36, 45, 56, 66, 69, 70, 89, 93–95, 100, 101, 105, 127, 163, 168, 174*). The spontaneous dissociation of hydrocarbon ions has been reported and some additional data on these metastable ions have been obtained (*12, 48, 64, 65, 101*). The difference in the dissociation probabilities of C–H and C–D bonds and of H_2 and D_2 have been investigated (*9, 41, 148*). Positioned isotopic tracers have been used to study the nature of the dissociation by electron impact and the mechanism of catalytic cracking (*57, 106, 149, 161*). A few of the many examples in which the mass spectrometer has analyzed the gases produced in various processes may be noted (*49, 71, 136, 167*). Eltenton has studied reaction intermediates by means of a mass spectrometer (*40*), and others are pursuing this field. Other methods of producing ions have been investigated, such as the production of ions from hot filaments and the formation of negative ions at surfaces (*77, 129, 141, 142*).

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ELECTRON MICROSCOPY

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DURING the past decade the electron microscope has grown from an extremely complex, highly specialized instrument, difficult to operate and maintain, with a resolving power not much superior to that of a visual microscope, into a simple instrument, capable of operation by relatively inexperienced personnel, and exhibiting a resolving power roughly 250 times greater than that of the best visual microscope. Indeed, the statement has been made (*86*) that the likelihood of obtaining higher resolving power —i.e., better than 8 Å.—is extremely remote, until an entirely new technical approach is made to the problem. This opinion should not, however, deter anyone considering possible applications of the instrument, for the dimensional range now available takes one virtually to atomic dimensions and provides adequate ground for research in almost any field of chemistry, biology, or physics.

With the conclusion of World War II, foreign firms have been able to resume active work in the design, development, and production of electron microscopes (*20, 43, 64–67, 69, 70, 95, 97, 107, 127*). These instruments are similar in most respects to those units familiar in this country. There appears to be some tendency toward the use of slightly higher accelerating voltages (80 to 90 kv.) in certain of these instruments, although the increase in electron penetration which can be expected would scarcely seem to warrant the additional electrical problems presented. Nevertheless, Van Dorsten, Oosterkamp, and le Poole (*146*) have completed an electron microscope capable of operation at 400 kilovolts and have shown that use of such high potentials makes possible the observation of certain structural details in relatively thick biological materials. The early results obtained with the European microscopes make it appear certain that foreign electron microscopists need no longer feel dependent on this country for satisfactory equipment.

Improvements are, of course, also being made on American equipment. Froula (*55*) has described attachments for simplifying the task of aligning console-type electron microscopes. Quynn (*129*) has described a device for mounting and adjusting an aperture in the objective pole piece of the RCA Type EMU microscope, which should aid considerably the process of alignment. Numerous patents (*8–11, 133*) have issued outlining improvements in electron microscopes and associated equipment, although the inevitable delays in patent prosecution imply that much of this material is either well-established practice or outdated.

Research on the theoretical and experimental aspects of electron-gun (*50, 91*) and eleeton-lens (*13, 25, 40, 41, 45, 89, 92, 100, 101, 106, 110, 114, 137, 142, 149, 157, 158*) design continues. To many practical electron microscopists, this work appears to be of little interest. Obviously, however, it is of fundamental importance in supplying the data which will be necessary for improvement of our present electron microscopes. Similarly, experimentation with proton microscopes (*24, 86*), ion microscopes (*15*), and theoretical considerations of other methods for improving the resolving power (*86*) are fundamental for the success of future work in this field. Of particular interest in this regard is the description by Gabor (*59*) of a new microscopic principle which dispenses entirely with electron objectives. Micrographs are obtained in a two-step process by electronic analysis, followed by optical synthesis as in the Bragg x-ray microscope. However, the Bragg technique is applicable only in very special cases, where the phases are known beforehand, whereas the principle suggested by Gabor provides a complete record of amplitudes and phases in one diagram and is applicable to a very general class of objects. Theoretical analysis indicates that an instrument incorporating this idea should be capable of a resolving power considerably greater than that of the usual electron microscope.

Many workers have been interested in studying the relation between lens defects and image clarity (*12, 14, 19, 87, 130*). Others (*16, 18, 28, 108, 132*) have concerned themselves with studies of the theoretical resolving power of an electron microscope as determined by the maximum available contrast in the images. A particularly important paper by Hillier and Ramberg (*87*) discusses the contour phenomenon in electron microscopical images near focus and suggests practical methods for minimizing lens defects so that the average microscopist may approach more closely the ultimate resolving power of his equipment. The popular and highly controversial subject of objective diaphragms is discussed in at least two papers (*48, 72*). In one of these Hall (*72*) suggests an ingenious multiple-objective aperture in which a piece of 200-mesh screen similar to that employed as a specimen mount is placed below and in register with the holes of the specimen screen, thereby providing an individual objective aperture for each opening of the normal specimen support.

Of perhaps greater importance, however, is the use of Hall's aperture device for production of dark-field electron microscopical images. This is a phase of research which has been sorely neglected, having been discussed in only a few publications during the past decade. Practical aspects of this work are considered by Hall (*73, 74*) in two highly informative papers. The first of these describes the use of dark-field electron microscopy for determining the degree of crystallinity of various substances and the second applies the technique to a study of colloidal carbon. It appears that these methods may be employed as extensively in electron microscopy of the future as they are in visual microscopy today. We now require only simplified techniques for making possible routine use of the method on any electron microscope.

Although in a reasonably satisfactory state, the problem of magnification determination in electron micrographs has been discussed again by Froula (*54*), and two techniques employing diffraction grating replicas as specimen mounts are described.

SPECIMEN PREPARATION

The subject of the preparation of substrates and specimens for electron microscopy has received some attention, although many of the techniques which are employed for preparation of various materials are considered to be in the nature of "classified material" by the organizations employing them. Obviously, this is unfortunate since much duplication of effort could be avoided if these methods were discussed publicly in greater detail. One particularly interesting development has been the use of metallic, rather than organic, substrates for specimen supports, as suggested by Hast (*80*) who employs thin (approximately 20 Å.) films of beryllium or aluminum. These films deserve wider application since when properly prepared, they are relatively structureless and capable of withstanding severe electron bombardment. Burton has used them with marked success in his laboratory. The use of silicate glass films has been suggested by Möllenstedt (*117*), and Ellis (*49*) describes a plastic film (Alkathene) which is resistant to many organic solvents. Drummond (*39*) has reviewed in a general way the standard methods of sample preparation and has discussed techniques for metal shadowing and smoke precipitation. Some observations on preparation of Formvar replicas and their interpretation, as well as a discussion of the structure of glass surfaces, both polished and fractured, on the basis of replica observations, have been made by Deacon, Ellis, Cross, and Sennett (*37*). Brown and Jones (*17*) have described a replica technique for wet specimens in which an initially viscous material (methyl methacrylate monomer) is allowed to flow over the specimen and polymerized in place thus involving no applied pressure and no rise in temperature; a silica film is then prepared in the usual way and is observed after dissolving away the plastic impression. A technique of a very different type is that proposed by Hunger and Seeliger (*88*) who suggest that hard metallic surfaces can be reproduced by making an impression in pure aluminum which after electrolytic oxidation yields a normal aluminum oxide–impression film which can be removed and examined electron microscopically. The preparation and use of conventional polystyrene-silica replicas have been the subject of a comprehensive paper by Gerould (*60*) who has taken great pains to describe his techniques in such a lucid and elementary fashion that the newest electron microscopist can have no excuse for not employing replica methods whenever necessary.

More specialized problems of specimen preparation are considered by Cravath (*33*) who discusses methods of pigment preparation and by Mateosian (*115*) who describes the necessary conditions for electrolytically polishing metal specimens. As an auxiliary piece of equipment for specimen preparation, an apparently useful device is a punch described by Grey (*63*) which can be incorporated in any standard light microscope so that the selecting, accurate centering, and the punching of a specimen can be performed in a single operation.

A considerable amount of research is being directed to a study of the causes and prevention of specimen contamination as a result of electron bombardment. All too frequently the possibility of such artifacts in electron microscopical images is either not recognized or is ignored. Numerous examples of this sort, particularly in biological studies, can be seen even in a casual study of the literature during the past ten years. It should be obvious physically that a beam of 50 to 100 kilovolt electrons can cause marked changes in heat labile materials and yet there has been infrequent discussion of this problem. Burton, Sennett, and Ellis (*23*) and Kinder (*96*) have shown that certain alkali halide crystals become transparent under electron bombardment and Mandle (*111*) demonstrated that similar effects occur in images of gold-shadowed tobacco mosaic virus. Claims that temperatures of the order of 264° to 278° C. exist at the specimen position are advanced by Ruess (*141*). These temperatures seem rather low since Watson (*153*) claims to have melted certain particles of titanium dioxide, thereby implying local temperatures of the order of 1600° C.

The mechanism of the degradation and contamination of specimens has been discussed by Watson (*152, 154*), Cosslett (*30*) and Hillier (*84*). Watson advances the hypothesis that "the growth is caused by the deposition as solids of hydrocarbon vapors polymerized under the bombardment and originating from locations inside the microscope." Cosslett feels that the specimen contamination is the result of deposition of charged metal and other particles ejected from the supporting grid by the electron beam. Hillier in a thorough analysis of the problem inclines in principle to the Watson hypothesis and suggests that the organic vapors arise by diffusion out of the metal walls, gaskets, and greases exposed to the vacuum. Judging from these divergent opinions as to the mechanism, the problem apparently still remains unsolved. However, the very fact that it is being considered so actively is commendable.

ELECTRON MICROSCOPE UTILIZATION

Technical Problems. Applications of the electron microscope to specific technical problems are, of course, widespread. The study of carbon black continues to be a popular field of research. Watson (*156*) has pointed out the possible existence of crystalline platelets in certain varieties of carbon black; Konig (*103*) has discussed the appearance of carbon droplets resulting from the coagulation of a graphite melt. Brusset (*21*) studied carbon black by combining the techniques of electron microscopy and small angle x-ray scattering and showed that the samples in each case were arranged in the same order but that the size determined electron microscopically was several times greater than that calculated from x-ray measurements. Anderson and Emmett (*3*) have compared electron micrographs and nitrogen adsorption isotherms for six commercial carbon blacks and come to the conclusion that the two methods for obtaining particle size and surface area measurements are in substantial agreement, except in the case of blacks known to be porous. The aging of gold and silver smoke deposits, before and after heating, has been considered by Roginskiĭ, Shekhter, and Sakharova (*140*) who show that the particle size distribution changes after heating. Harris, Jeffries, and Siegel (*78*) have measured size and distribution of particles in gold smokes. Two papers (*47, 52*) describe the examination of lubricating greases and discuss in terms of lubricating properties the beautiful fibrous structure which is brought out as a result of metal shadowing of the material. A pictorial record of melting glass mixes and soda slag from room temperature to 1500° C. has been presented by Endell and von Ardenne (*51*). Fullam and Savage (*57*) investigated carbon film formation and commutator brush wear in electric motors and showed that the surface consists of many tilted "fingers" which are the projecting portions of the large and irregular graphite plates comprising the brush.

Examinations of asbestos fibers have been reported by two groups (*102, 121*) and the structure of clays has been studied by Hast (*79*) using thin beryllium aluminum replicas. Shekhter, Roginskiĭ, and Sakharova (*143*) have described an investigation of precipitates freshly formed from solution, and their work indicates that in the case of highly insoluble deposits there appears a predominance of rounded forms with no sharply defined angular forms. A general study of catalysts, bleaching clays, bentonites, and schists has been published by Alais, de Fouchecour, and Reis (*1*) who note that fresh catalysts show much greater dispersion than used ones. Uses of the electron microscope in the paper industry are discussed by Uchastkina (*145*), and Walton (*150*) describes its application to the measurement of particle size. The application of the technology of "resinography," a term which embodies the general study of the structure of resins including the identity of its phases (*139*), has been described by Rochow, Coven, and Davis (*138*) with particular emphasis on problems of the paper industry. A note (*5*) from the National Bureau of Standards describes a low pressure–low temperature replica technique for the examination of wool fibers. Hamm and Comer (*76*) have devised a replica method for studying dyed nylon fibers which comprises transplanting the dye crystals from the surface of the nylon fiber to the replica. The silica-dye crystal combination is then interpreted as though the original dyed fiber were being examined. Two interesting papers by Watson (*151, 155*) discuss studies of gases polymerized by charged particle bombardment and apparently show rather marked differences in the appearance of the polymer depending on the type of radiation used to bring about reaction.

Metallurgical Problems. Strangely enough, there have been very few papers devoted to metallurgical problems, reflecting no doubt the skepticism which still exists in the minds of many metallurgists concerning the validity of the replica techniques which must be employed for such studies. This is not surprising for the subject of replica interpretation is still a matter for active discussion. The situation will probably not improve to any great extent until a detailed comparison is made at the same magnification of the structures seen in an optical metallograph and the same structures as reproduced in replica form and examined electron microscopically. Recently a very ingenious approach to this problem has been suggested by Bryner (*22*) who proposes a technique employing a specially prepared specimen screen to aid in locating the same field in both light and electron microscopes. It is hoped that widespread use of this or similar methods will aid in correlating more completely data obtained from visual and electron microscopical studies of the same specimen. Two general papers (*38, 68*) discuss the significance of the electron microscope in metallurgical work. In addition, Heidenreich and Schockley (*82*) have applied the techniques of electron microscopy and electron diffraction to the study of slip in metal crystals.

Biological Studies The electron microscope is used extensively in biological studies. The Massachusetts Institute of Technology group under the direction of Schmitt has continued to be very active and produces such outstanding work that it occupies a pre-eminent place in the field. Three papers (*75, 93, 94*) from this group discuss observations of actin and myosin and studies of the trichocysts and cilia of the paramecium. Several other groups have made studies of a similar nature: Ranzi (*134*) has investigated the action of salt solutions on myosin; Nutting and Borasky (*120*) have examined collagenous fibers in an effort to determine the mechanism of leather tannage; Hawn and Porter (*81*) have studied the fine structure of clots formed from purified bovine fibrinogen and thrombin; Reed and Rudall (*135*) have examined collagen and muscle structures in an effort to study the degree of organization in cells; Passey, Dmochowski, Astbury, and Reed (*123*) have photographed electron microscopically tissues and extracts of tissues and tumors of high cancer strains; Matolsky (*116*) has examined renosine, the structure protein of the kidney, and has shown the presence of filaments which tend to branch and split longitudinally; and Mossman and Noer (*118*) have published a study of amnion.

The structure of cells, despite the difficulties of specimen preparation and image interpretation, still occupies the attention of numerous workers. Chicken tumor cells and rat sarcoma cells have been examined by Claude, Porter, and Pickels (*26*) and by Porter and Thompson (*128*), respectively. The techniques used by these groups for the preparation and mounting of tissue culture cells are particularly noteworthy. Chloroplast structures have also been studied (*2, 62*) and numerous interesting observations are described. Eisenstark and Clark (*46*) have published electron micrographs of x-ray treated cells.

Several papers (*44, 104, 131, 147, 148*) describing bacteriological studies have appeared. One of these (*147*) is particularly interesting in that it shows the excellent resolving power of the Delft electron microscope. Virus studies have been made by a number of workers (*34, 36, 109, 112, 113, 124, 144*). Anderson, Boggs, and Winter (*4*) discuss the relative sensitivities of bacterial viruses to intense sonic vibration and show that the sensitive viruses with their large and complex structures are disintegrated by intense mechanical vibration whereas the small, compact viruses are relatively resistant. Oster and Stanley (*122*) have measured the minimal infective virus units in hair cells of tobacco leaves which have been infected with tobacco mosaic virus.

In concluding this brief biological review some mention should be made of microtome techniques. The high-speed rotary microtome has endeavored to secure a place as an important adjunct to electron microscopy. Unfortunately, however, it cannot be said that the device has attained such a position. It is a complex piece of apparatus, is expensive, and to date has produced no published results which can be considered outstandingly important. That the development should continue, however, there can be no doubt, for the introduction of satisfactory microtome techniques would open broad new fields in biology and fiber technology. In this connection, a particularly important paper has been published recently by Pease and Baker (*125*) who describe sectioning techniques for electron microscopy using a conventional microtome. These workers have been able to cut consistently 0.2-micron sections sufficiently thin to allow adequate electron penetration. Their preliminary results indicate that the method should receive widespread attention.

ELECTRON DIFFRACTION

The inclusion of several papers on electron diffraction in this review can be justified by the close relationship of the two techniques. As the technology of electron microscopy advances it becomes increasingly apparent that the instrument cannot be used without recourse to other methods and equipment. A particularly useful auxiliary technique, and one which can be practiced on almost any electron microscope without major modification, is electron diffraction. Although electron diffraction as a technique is somewhat older than electron microscopy it has in the past been primarily associated with, and to some extent overshadowed by, the more versatile technology of x-ray diffraction. Now that it is possible to obtain electron micrographs and electron diffraction patterns of the same specimen (*35*) the use of electron diffraction should become more widespread and should provide information which may aid materially in the interpretation of electron microscopical data. Inundi (*90*) has described an arrangement of lenses which purports to exhibit advantages for electron diffraction work; Picard and Reissner (*126*) have described a method of operation to allow use of the RCA universal electron microscope as a high resolution electron diffraction camera; Dunaway and Barton (*40*) have described an electron diffraction specimen holder for use with this same instrument. Electron microscopists who become familiar with and make use of auxiliary methods of this kind will be doing themselves and their science a service.

DISCUSSION

Various instruments for simplifying electron microscopical work are occasionally described. Thus, for accurate exposure of electron micrographs Müller (*119*) has outlined a device which consists of an electric shutter connected to a photoelectric exposure meter. Another clever instrument is one designed by Hanson and Daniel (*77*) for measuring particle diameters and constructing histograms from electron micrographs.

A number of reviews covering various phases of electron microscopical work have appeared. These range from rather elementary discussions (*7, 27, 53, 56, 61, 71, 85, 136*) designed especially for popular consumption to more comprehensive reviews like those of Wyckoff (*159*), Hillier (*83, 86*), Kushnir (*105*), Cosslett (*32*), and Dupouy (*42*), which are directed to scientific personnel and which attempt to describe in some detail the present state of the art and the possible direction of future research. In addition, Kirchner (*99*) has presented a very interesting historical account of the discovery of the electron, electron waves, and electron lenses. A monograph by Gabor (*58*) purports to be "an up-to-date report on this comparatively new instrument including a survey of application, laboratory technique, theory of image formation, latest commercial types, and future trends." This book is of particular interest to American electron microscopists in supplying some information, even though of limited scope, regarding European electron microscopes, their general operating characteristics, claimed resolving powers, etc. It is gratifying that the historical account of the development of electron microscopy places considerably more emphasis on the fundamental European work than is the case in some American presentations. Finally, there is an excellent chapter evaluating methods which have been proposed for improving the ultimate resolving power of the microscope.

The American and British Electron Microscope Societies are active, as evidenced by the appearance of several reports (*6, 29, 31, 98*) describing their programs. These groups have contributed much to the progress of electron microscopy by providing a common meeting ground on which scientists can discuss their problems, describe new techniques, and consider the proper interpretation of their data.

From this brief review of work carried out primarily during the last 24 months, it must be obvious that electron microscopy is still making rapid strides. Indeed, it is difficult to realize that the science is only 15 years old since its earliest conception, and that most of the advances in application of the technique have been made during the latter half of this period. The enthusiasm of the early popularizers of the equipment has fortunately been tempered to a large extent and even its most ardent supporters no longer consider it a panacea. The electron microscope is properly finding its place as an adjunct to the older sciences of visual microscopy, x-ray diffraction, and spectroscopy. It supplies information of a type not available from any of these other scientific methods and yet without their assistance its information is frequently barren. Nevertheless, it has proved a tool of immeasurable value and its future prospects of application appear bright.

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LIGHT MICROSCOPY

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THE Symposium on Light and Electron Microscopy held in Chicago (*3*) served to emphasize that the very rapid expantion and development of electron microscopic techniques have served to stimulate further interest in light microscopy. Many of the papers presented at the symposium stressed the correlation of electron and light microscopy (*65*). Other publications which compare the results given by light and electron microscopy include the study of pigments (*32, 135*) and of metals (*35*). Pijper (*110*) describes a dark-field study of typhoid bacillus in which sunlight was used as an illuminant; the results, recorded on motion picture film, show that what has been considered for many years to be active bacterial flagella really are passive mucous twirls.

One of the important contributions which electron microscopy has made to light microscopy is the replica technique. Although replicas had been used in light microscopy before the days of the electron microscope, it needed the recent work with the electron microscope to develop the refinements in technique which have made the replica so important in present-day research. Schaefer proposed making replicas containing dye for use with the optical microscope (*122*). The metal shadowing technique worked out by Williams and Wyckoff (*145*) is proving to be very important for light microscopy. According to this publication, satisfactory replicas are obtained with collodion, Formvar, and Faxfilm, and aluminum is a suitable metal for shadowing these replicas for optical microscopy. This technique gives a very high contrast image, so that the microscope objectives may be used at their maximum resolving power. The application of the shadowing technique in the preparation of replicas of tooth surfaces is described by Scott and Wyckoff (*125*). The application of replica techniques to the study of ceramic surfaces with the the optical microscope is described by Allen and Friedberg (*1*).

Another technique, which was developed for electron microscopy and is also applicable to light microscopy, is the use of the high speed microtome for cutting extra thin sections of biological and other material (*39, 55, 57, 106, 124*). The paper by Seidel and Winter (*126*) has deepened the mystery as to exactly what has been achieved by Rife in his universal microscope. The article states that this marvelous instrument, which has a resolving power greatly surpassing theoretical limits, contains 5862 parts, but does not give an adequate description of the parts or a scientific explanation of their function. As Rife has not published details of the construction and principle of his microscope, it is to be hoped that a group of selected scientists will have an opportunity of investigating it, so that the scientific world in general can be given an accurate appraisal, and optical theory be reinvestigated if necessary.

A new microscopic principle has been described by Gabor (*56*), according to which a point source of radiation is made to yield a complex diffraction pattern of the object. This diffraction pattern is photographed and subsequently unscrambled by optical means to yield an enlarged image of the object. It is believed that this method will be of use in electron microscopy, but its possibilities in light microscopy remain to be determined.

TRANSMITTED LIGHT

Microscopists have long been troubled with the necessity for changing the illuminating system of the microscope when working alternately with low and high powers. If the microscope is set up to give Köhler illumination with a high-power objective, changing to a low-power objective with the same condenser gives a very small illuminated field, so that some sort of auxiliary illuminating system or condenser is necessary if the microscopist is to leave the Köhler system in proper alignment. Benford (*21*) has described a substage condenser which can be used for high powers, low powers, and dark-field illumination, in which the illuminated field corresponds to the field of view of the objective.

Another attempt to achieve a more or less universal condenser is described by Hall (*64*), in which the microscope is equipped with a variable-focus condenser. This condenser, which is a two-lens Abbé type, has the top lens fixed to the microscope stage. The bottom lens is racked to its top position with a high-power objective, and to its bottom position for low-power objectives. A condenser of this type is considered adequate for much student and industrial work. In using the Köhler system of illumination, when the system has been properly set up, and the substage diaphragm has been opened to give a 4/5ths cone of light in the objective, the illumination is usually very much too bright for comfortable work, and its intensity must be reduced by means of a filter. Benford (*21*) has described a set of Inconel neutral filters for this purpose which are said to be very good for color photomicrography. Copeland (*40*) has described the adaptation of a Polaroid variable-density filter from an American Air Force gun sight for this purpose. By merely rotating one of the component polarizers the intensity of the light can be adjusted to a comfortable working value. Dempster (*47*) has given a detailed discussion of microscope illumination with special reference to the problem of glare of both optical and visual origin.

REFLECTING MICROSCOPES

The ultraviolet reflecting microscope of Burch (*36*) has been applied to the study of nuclear plates (*18*), where its very great working distance has proved very useful. Bouwers (*27, 28*) has described a simple reflecting microscope, which is already used in some European schools.

INCIDENT LIGHT

A combined vertical and concentric opaque illuminator has been described by Benford (*21*). The reflector consists of glass coated with titanium dioxide on one side and magnesium fluoride on the other. A swing-out dark-field stop allows the light to travel either down the objective when the customary bright-field vertical illumination is obtained, or down a plastic paraboloid surrounding the objective, which gives the so-called dark-field type of incident illumination.

Hauser and leBeau (*70, 71*) have described an important application of the concentric opaque illuminator. Using a Leitz Ultropak they adapted the electron microscopic technique of mounting specimens on wire gauze for the study of lyogels in the vulcanization of rubber, and applied the method to the study of structural changes of natural and synthetic rubbers during mastication and the subsequent recovery process (*87*). Hauser's work emphasizes the value of rendering an object self-luminous as a means of obtaining the highest possible resolving power of the microscope.

DARK-FIELD ILLUMINATION

Attention has been attracted by the method of "optical staining." According to this technique, which is described by Crossmon (*44, 45*) and Dodge (*48*), the material to be studied is mounted in a liquid having a much higher dispersive power but preferably the same refractive index as the material for some specific wave length of light. The preparation is examined by dark-field illumination. Substances of different refractive index may be readily differentiated by this means. One of the examples given is that of corundum mixed with other mineral grains, with methylene iodide as an immersion liquid. Under dark-field illumination, corundum appears bright yellow with purple borders, sharply contrasting with the whites and blues of the other mineral grains. Ultramicroscopy in color has been described by Hauser (*69*).

PHASE CONTRAST MICROSCOPY

There has been considerable activity during the past few years in the relatively new field of phase contrast microscopy. The general principle is described by Zernike (*149*) and in a recent translation of the paper by Köhler and Loos (*82*).

An annular diaphragm is placed below the substage condenser to provide a hollow cone of illumination. The internal and external diameters of the annulus are such that the image of the annulus in the rear focal plane of the objective extends from approximately one half to approximately three quarters of the full aperture of the objective. A disk is placed at the rear focal plane of the objective, which is referred to as a "diffraction plate" or "phase plate." It has an absorbing annulus which cuts down the intensity (or amplitude) of light which is not diffracted or deviated by the object through which it has passed; in addition, a phase difference is introduced between this direct beam and the inner and outer diffracted, or deviated, beams by adding a transparent coating of appropriate thickness either to the absorbing annulus or to the clear inside and outside zones. The light through the annular zone and that through the rest of the objective interfere when combined in the microscope image to give either bright or dark detail. A variety of effects, both bright contrast and dark contrast, can be obtained by changing the intensity and phase relationships between the direct and deviated light.

Burch and Stock (*37*) described a phase contrast microscope constructed in 1942. Richards (*114*) described progress being made at the American Optical Company plant. Linfoot (*89*) referred to the work of Burch and mentioned that the phase plates were being made with evaporated coatings which could be cut with a stylus to give zones of accurate dimensions. Bennett, Jupnik, Osterberg, and Richards (*22*) described further advances being made by the American Optical Company, and experiments with phase plates having various amplitude and phase relationships. Brice and Keck (*29*) also studied the question of the most favorable absorption of the phase plate.

Considerable attention has been devoted to trying to produce a variable-phase contrast system for microscopy whereby it would be possible to change from bright to dark contrast at will, and to change the phase relationship also. Hartley (*67*) described a combination of a quarter-wave mica and polarizing device. A device utilizing right- and left-handed quartz was described by Taylor and Payne (*109, 132, 133*). A device employing polarized light which gives both variable phase and variable amplitude has been described by Osterberg under the name of the Polanret microscope (*107*). A device using a combination of half-wave and quarter-wave plates is described by Kastler and Montarnal (*77*). Osterberg (*108*) has also studied the application of the principle of the multipupil in phase contrast microscopy, and has concluded that phase contrast accessories could be placed at optical equivalents of the rear focal plane of the objective, whereby a simplification in construction might be effected. Bennett, Woernley, and Kavanagh (*23*) have described preliminary work with an ultraviolet phase contrast microscope which employs a 16-mm. reflecting objective. Other optical parts, such as the condenser and diffraction plate, are made from fused silica.

Phase contrast microscopy is proving of considerable value in the study of transparent objects having a small refractive index difference from that of their mountant. Among applications described in recent literature are textile fibers (*112*), viruses (*17*), cell cultures (*150*), and mineralogy (*128*). It is also possible to apply phase contrast methods to metallography with vertical illumination (*46*, *76*). General discussions of phase contrast microscopy have been given by Lachenaud (*83*), Michel (*100*), Salmon (*121*), and Martin (*95*).

INTERFERENCE MICROSCOPY

A number of new contributions to the interferometric study of crystals have been made by Tolansky (*136*). Merton (*98*, *99*) has described a promising new method of interference microscopy in which the specimens are mounted between half-platinized surfaces. The optical system of the microscope comprises a zone plate beneath the condenser and a corresponding zone plate in the rear focal plane of the objective. The zone plates must have the same order of interference as the half-platinized cell. Either a single wave length of monochromatic light or two wave lengths bearing a simple arithmetical relationship are used. This method is not the same as phase contrast microscopy, and may yield information which cannot be obtained by the latter. Zone plates are said to be available from A. Hilger of London. Ambrose (*2*) has described an interference microscope for the study of inhomogeneous media. Kayser (*78*) has described an interference band method of checking surface finishes. Jelley (*74*) has described an interference method for the comparison of crystalline substances.

FLUORESCENCE AND PHOSPHORESCENCE MICROSCOPY

A simple fluorescence microscope and its use in the detection of bacilli which stain with fluorescent dyes have been described by Richards (*113*). Jailer (*73*) has used the fluorescence microscope in the study of the physiological distribution of atabrine. Strugger (*131*) has described the present status of fluorescence staining of bacteria with particular reference to the use of Acridine Orange and Brilliant Sulfoflavin. A very good photomicrograph showing the specific staining of the spores of *B. mycoides* is given. A method of photographing very weak fluorescent spectra has been described by Scheminzky (*123*).

Harvey and Chase (*4*) have used the principle of the Becquerel phosphoroscope with a microscope for the study of the phosphorescence of biological materials.

ULTRAVIOLET MICROSCOPY

A simple construction for a quartz ultraviolet microscope illuminant has been described by Lavin (*86*), in which a Hanovia lamp is enclosed in a Transite box under the microscope. A translation of a Soviet paper on the use of the ultraviolet microscope in the study of living and dead cells has just appeared (*85*). Foster and Thiel (*53*) have described a fused-silica fluorite achromatic ultraviolet objective having a focal length of 2.5 mm. and a numerical aperture of 0.85.

Considerable progress has been made in England by Burch (*36*) with his ultraviolet reflecting microscope. A description of the system used by Burch together with some surprisingly good photomicrographs taken with the instrument are given by Barer (*16*). The research laboratories of the Polaroid Corporation are developing a reflection microscope for the study of ultraviolet absorption of cell components. The principle of "color translation" is used in the presentation of the photomicrographs in which photomicrographic negatives obtained with three different wave lengths in the ultraviolet are printed in register with the three subtractive colors used in ordinary color photography. This gives an interpretation in color of differential absorption in the ultraviolet (*84*).

INFRARED MICROSCOPY

Bailly has described the use of infrared-sensitive photocells in the identification of opaque minerals (*13*, *14*). The use of the now-familiar infrared image tube in seeing through the microscope with infrared light is described by Morton and Flory (*103*).

GENERAL

Two accessories for use with the dissecting microscope are a chin-operated focusing device (*72*) and a portable light (*146*). Two outstanding books in the field of general microscopy are by Shillaber (*127*) and Wredden (*147*).

CRYSTALLOGRAPHIC MICROSCOPY

Recent improvements in the optical characteristics of Polaroid polarizers and analyzers have resulted in the producton of excellent petrographic microscopes using this type of polarizer in place of the Ahrens prisms formerly used but which are now becoming scarce on account of the difficulty in obtaining calcite of high optical quality. Another type of polarizer has been patented by Dreyer (*51*). According to the patent specification, melts or solutions of dyes capable of forming a nematic phase are deposited on a previously oriented surface, such as that produced on glass by buffing. Polarizers of this type might find special applications in phase contrast microscopy. A universal stage accessory for the investigation of small crystals and jewels has been described by Waldmann (*141*).

Three hot stages for use with the microscope have been described in the period under review. Bonner (*26*) has constructed his so that it will take 1 × 3 inch microscope slides which may be moved or changed while the stage remains hot. Vold and Doscher (*138*) have given particular attention to the problem of maintaining a uniform temperature over a large area with a heating rate of 1.5° to 2.0° C. per minute. Efficient heat insulation is obtained by using a Johns-Mansville magnesia brick in the construction of the stage; when the specimen is heated to 350° C., the outside of the stage is only faintly warm. A second design, with a built-in-air-circulating fan, gives a very low temperature gradient in the specimen chamber. Matthews (*97*) constructed a stage consisting essentially of an electrically heated copper block surrounded by a water jacket through which water at 25° C. is circulated. Three advantages are gained by having the constant-temperature water jacket around the heating unit: The microscope is protected from undue heating; the stage may be cooled rapidly; and the rate of heating is strictly under control, so that a given amperage will give a reproducible rate of heating and maximum temperature. Matthews' method of using the stage takes full advantage of this reproducibility.

Thermal methods for the identification of organic compounds are coming very much to the front. The pioneers in this field are L. and A. Kofler, whose contact method of studying the formation of eutectics and mixed crystals was described in two papers which were not generally available in this country during the war (*79*, *80*). Their methods of thermal analysis have been incorporated in a book recently published in Innsbruck, Austria (*81*), and at present being translated by McCrone (*92*). Reimers (*111*) discusses the advantages and limitations of thermal analysis. Fusion methods have received considerable study by McCrone and his collaborators (*58*, *59*, *91*, *93*), who have worked out a method of determining *p,p'*-DDT in the technical grade of material, and have studied the kinetics of crystal growth from the melt of binary mixtures. A comparison slide technique for comparing the optical properties of a known with an unknown substance is given by Jelley (*74*). Recommendations and advice on the correct presentation of crystallographic data for publication are given by Mason (*96*). A microscope goniometer has been described by Donnay and O'Brien (*49*). Bryant and Mitchell (*34*, *102*) have continued their study of the optical properties of organic compounds as a function of wave length for the purpose of providing ready means of identification.

An important new project has been started by the Armour Research Foundation under the direction of W. C. McCrone. Organic compounds of industrial or other importance are being exhaustively studied by x-ray crystallography, goniometry, and optical crystallography. It is proposed that the Armour Research Foundation serve as a clearinghouse for data submitted by other workers who may have neither the time nor the facilities to make complete determinations of all the optical properties of substances in which they are interested. Among the substances so far described are DDT (*5*), adipic acid and *trans*-azobenzene (*6*), ethylenediamine *d*-tartrate and dipotassium tartrate hemihydrate (*7*), *p*-methylaminophenol sulfate and *p*-aminoazobenzene (*8*), thiamine hydrochloride (*9*), α-pyridine sulfonic acid (*10*), β-pyridine sulfonic acid (*11*), and ascorbic acid and 1,3,5-tri-(*p*-chlorophenyl) benzene (*12*).

The composition and optical and crystallographic properties of two calcium oxylate calcium chloride double salts have been described by Jones and White (*75*). Waldmann (*142*) has given a new graphical method for determining the equation for the axial angle. Bruun and Barth reported that some of C. D. West's liquids of high refractive index, which were stored under water, have scarcely changed in 8.5 years (*33*). West has described the method of determining $n\alpha$ and $n\gamma$ used by his students (*143*). An account of the state of aggregation of some paraffin chain compounds is given by Vold and Vold (*139*). Neuerburg (*104*) has given a description of optical figures obtained by the use of polarized light in conjunction with a vertical illuminator. No explanation of the formation of these figures with opaque minerals is given, but it is considered that they might be of use as a means of identification. Subsequently, Neuerburg (*105*) found that the accidental birefringence of objectives alters the character of the figures. These reflection figures are of a very complex nature and do not in any way correspond to the convergent polarized light interference figures seen with transparent crystals. A brief account of some applications of optical crystallography has been given by Hartshorne (*68*), who is preparing a new edition of his "Crystals and the Polarising Microscope" (*42*). Three books of interest to chemical microscopists have been published recently (*74*, *137*, *140*).

MISCELLANEOUS METHODS AND APPLICATIONS

Publications in this field include the following: separation of crystals from gums on a micro or semimicro scale (*15*); dispersion of pigments and fillers used in the paper trade (*101*); dehydration of biological material by a diffusion process (*90*); use of acetic acid and sodium chlorite in maceration of woody tissue (*129*); and use of polyvinal alcohol for clearing and mounting biological specimens (*50*). Particle size determinations and analysis are dealt with (*31*, *52*, *61*, *144*). Chayes (*38*) conducts petrographic analysis by fragment counting. Microhardness testing in metallurgy (*30*, *130*), a new microindenter for use with a metallurgical microscope (*43*), and a simple and accurate microhardness testing device (*24*) are applications in the metallurgical field. Among technical applications may be mentioned the microscopical and x-ray examination of some steatite bodies (*115*), and the microscopy of high temperature phenomenon in ceramics (*19*).

In the textile industry, in addition to the work with the phase contrast microscope already discussed, publications include the application of microscopy to the control of quality in dyeing and finishing (*118*); other applications to the textile field (*119*) are discussed by Royer and Maresh. According to Bendigo (*20*), the microscope is becoming increasingly useful in textile work. His publication is illustrated with some striking color photomicrographs. A new microscopical test for the detection and estimation of damage in jute fibers is correlated with certain chemical tests (*94*). A method of determining the number of fibers above 0.1 mm. in length in a given amount of wood pulp has been developed and is used as a means of estimating the weighted average length of the fibers (*63*).

A microscopical study in connection with the extraction of rubber from goldenrod is discussed by Rollins and his collaborators (*117*). Quantitative methods of investigating plankton are given by Ruttner (*120*). In view of the fact that publications on a microdiffusiometer and its applications, relating to work carried out in the University of Prague from 1925 to 1938, are not generally available, Fürth has published a condensed account with a bibliography (*54*). Zapffe and Clogg have described a new method of metallurgical research in which microscopy combines with other methods of studying crystal faces at fractures caused by fatigue, corrosion, etc. (*148*). According to Lebeaux, the petrographic microscope has presented a new concept of freezing (*88*). Applications in chemical analysis include identification of ultramarine blue in complex pigment mixtures (*25*); as an aid in determining lime-silica ratios in blast furnace control (*41*); and identification of free silica in dusts and fumes by light as well as electron microscopy. According to this method, samples are collected on nitrocellulose supports, and are fumed over 48% hydrofluoric acid. The fumed specimen is then compared with an unfumed control. With this treatment, silica disappears whereas alumina remains (*60*). The microscope has been used in detecting particles of cadmium oxide in lung tissue (*134*).

RESINOGRAPHY

T. G. Rochow has proposed the name of "resinography" for the graphic study of resins and their plastics, analogous to "metallography" and "mineralography." In this field, the optical microscope naturally plays a big part, and all the methods of illumination, including the use of polarized light, may be employed (*116*). The microscopic examination of reinforced plastics is discussed by Gordon (*62*), while Harlow has investigated the microstructure of high density plywood (*66*).

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Polarographic Theory, Instrumentation, and Methodology

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PUBLICATIONS on polarographic analysis did not begin to appear in American journals until 1937, at which time the subject had already enjoyed 15 years of active growth in Europe and about 300 papers pertaining to it had been published in foreign periodicals, including the well known monographs by Semerano (*99*), Heyrovský (*31*), and Hohn (*36*). The first monograph on polarography in English did not make its appearance until 1941 (*46*), and by that time the publications in the field numbered nearly 900. During the intervening 8 years the bibliography of the subject has increased to more than 1500 titles and the task of keeping abreast of these has assumed Herculean proportions. This task has been lightened in no small measure by the excellent bibliographies which Heyrovský is continuing to publish (*30*), and by the bibliographies gratuitously being distributed by the Leeds & Northrup Co. (literature up to 1941), and the E. H. Sargent Co. (literature up to 1945). The present well established status of polarography in modern analytical practice is demonstrated by Strong's recent statistical survey (*106*) of all research papers published in the field of analytical chemistry during 1946 which places polarographic analysis among the five most popular "instrumental methods."

In preparing this report of polarographic developments during the past five or six years it has not been feasible to provide a comprehensive review of all of the several hundred pertinent papers. Therefore the treatment is limited to those innovations in theory, instrumentation, and methodology which indicate the lines along which the subject is currently developing. It has not been possible to discuss the many recent papers dealing with orthodox applications of polarography in practical analysis, but these may be located readily in the bibliographies referred to above. The excellent reviews of amperometric titrations by Stock (*104*) and

Figure 1. Sargent Visible Recording Polarograph, Model XXI

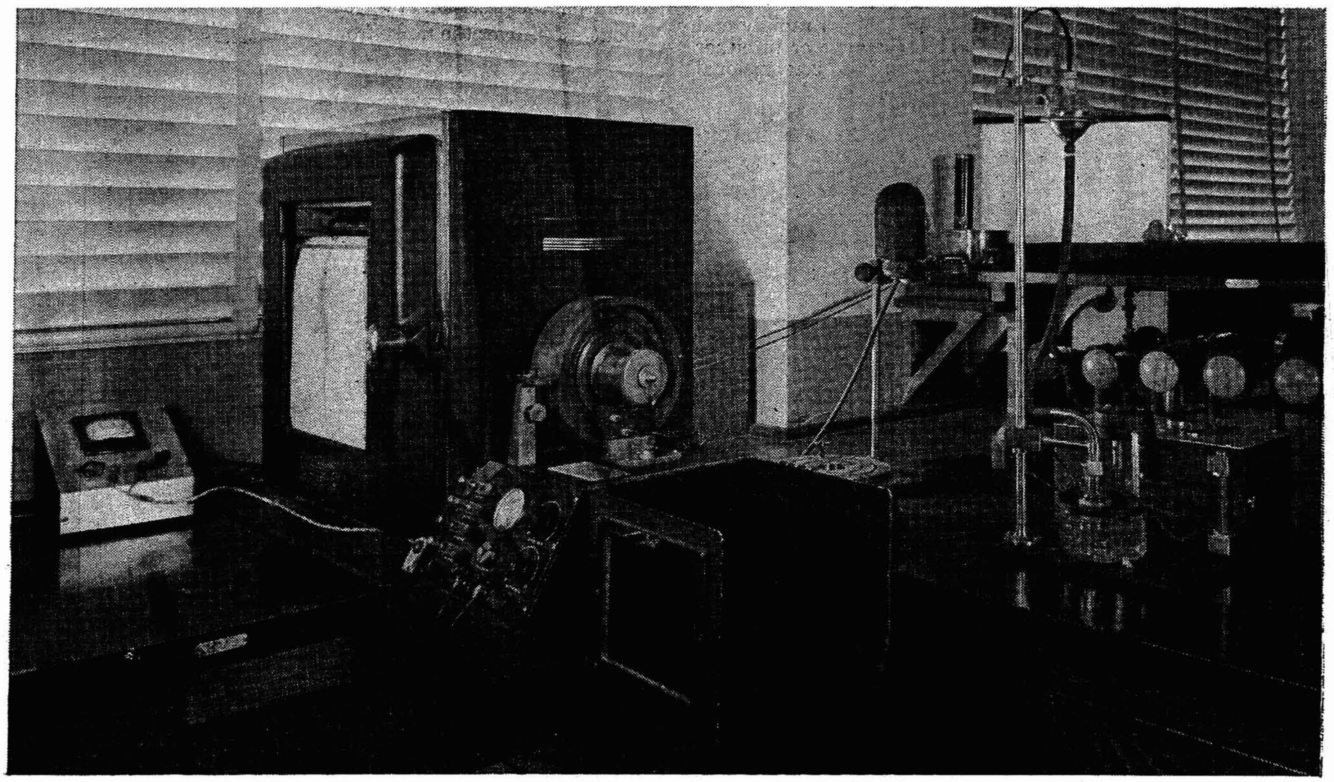

Figure 2. Complete Lykken-Pompeo-Weaver Polarograph (*73*)

Kolthoff (*42*) should be consulted for recent developments in this important branch of polargraphy. Those interested primarily in organic polarography will find the recent review by Müller (*83*) most helpful.

INSTRUMENTATION

POLAROGRAPHS

E. H. Sargent and Co. has developed a visual recording polarograph, the latest model of which is shown in Figure 1. The recording unit is a Brown Electronik potentiometer recorder, and the current is recorded in terms of the iR drop across a known resistance in series with the polarographic cell. The operating characteristics of the first model of this instrument have been discussed by Lingane (*63*), and the newer Model XXI utilizes essentially the same operating principle. However, many of the unsatisfactory characteristics previously noted (*63*) with the original instrument have been eliminated by a greatly improved circuit design and high quality components. The new instrument has been carefully designed and very well engineered in all respects. It is especially well suited for industrial laboratory use.

The polarograph shown in Figures 2 and 3 was designed by Lykken, Pompeo, and Weaver (*73*) in order to retain the great simplicity and reliability of direct galvanometer recording and yet to provide the convenience of a visible record.

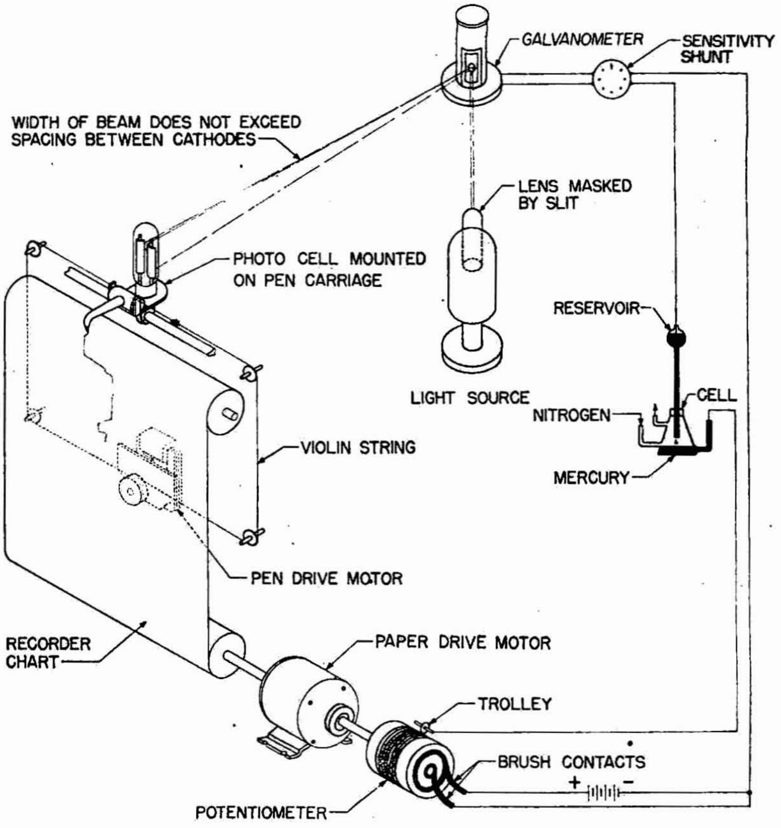

Figure 3. Schematic Diagram of Lykken-Pompeo-Weaver Polarograph (*73*)

The ingenious "photopen" recorder employs a double cathode phototube (R.C.A. No. 920) mounted directly on the pen carriage. By means of intermediate electronic relays the phototube signal is made to control the direction of rotation of the electric motor which drives the pen carriage. The motor remains at rest as long as the light beam from the galvanometer is focused between the two cathodes of the phototube, but the slightest movement of the beam activates one or the other side of the phototube, and the pen rapidly and faithfully follows the movement of the galvanometer in either direction. The remainder of the circuit follows good conventional practice.

In this writer's opinion the excellent performance characteristics of this instrument, combined with relative simplicity and great flexibility for all types of polarographic measurements, make it one of the best visible recording polarographs yet designed.

Schulman, Battey, and Jelatis (*98*) developed a visual recording polarograph with an undamped, high speed recording system.

A more or less conventional polarizing unit is employed. The current is amplified electronically and finally recorded on an Esterline-Angus recorder. The recorder gives full scale deflection in about 0.5 second, which response is sufficiently rapid so that something approaching the true current-time curve during the formation of individual drops is obtained. Provision is also made for conventional damped operation. This polarograph is marketed under the pseudonym Polaro-Analyzer by the Rutherford Instrument Co., Alexandria, Va., and is shown in Figure 4.

Schulman, Battey, and Jelatis recommended measurement of the maximum recorder oscillations, and with cadmium ion in 0.1 M potassium chloride they found a ratio of the maximum to average current of 1.24. This agrees approximately with the theoretical $^7/_6$ predicted by the Ilkovič equation. The alleged increased sensitivity that results from measurement of the maximum rather than the average of the undamped recorder oscillations is more or less illusory, because the residual current in terms of maximum oscillation is also larger.

The high speed, undamped recorder permits the use of rather high rates of voltage change (up to about 0.8 volt per minute) without much distortion of the wave form, and this may be advantageous in some studies. Judging from data with cadmium ion given by Schulman, Battey, and Jelatis, the instrument measures half-wave potentials accurately, and with undamped operation the precision of the current measurement appears to be about ±3% over the range from 0.2 to 100 microamperes.

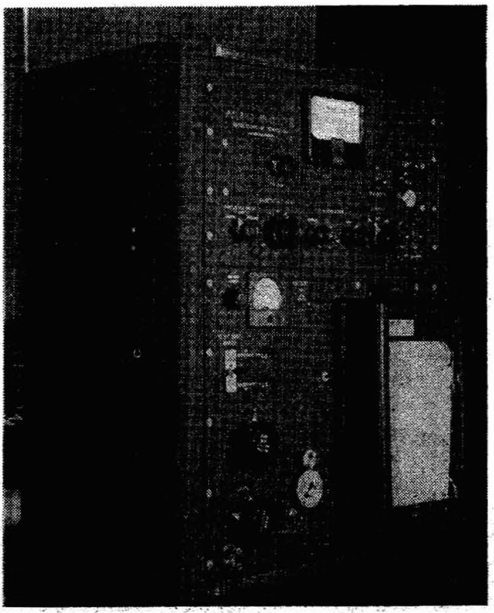

Figure 4. Polaro-Analyzer of Rutherford Instrument Co.

Polarograph based on original Schulman-Battey-Jelatis instrument (*98*)

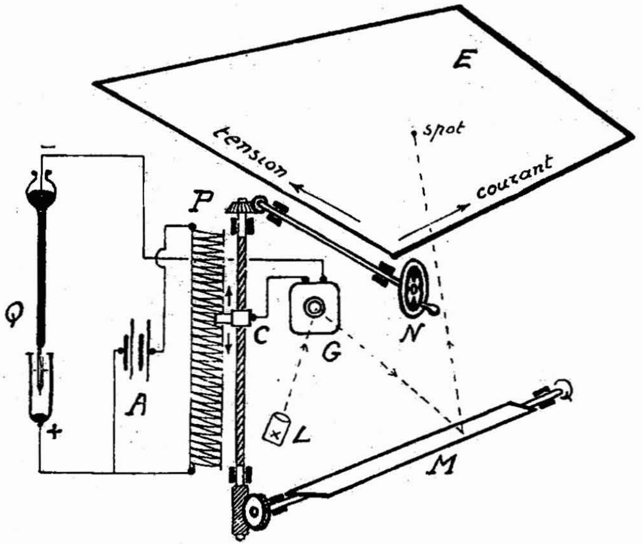

Figure 5. Principle of Breckpot Manually Operated Polarograph

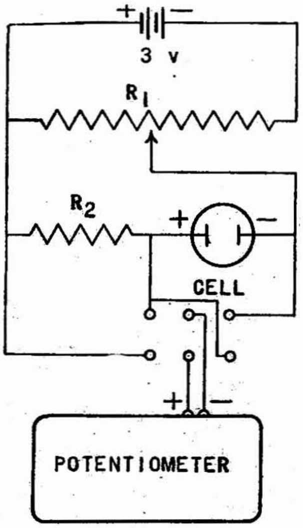

Figure 6. Simple Manual Circuit for Polarographic Analysis and Amperometric Titrations

Hohn (*37*) invented a rugged recording polarograph suitable for industrial laboratories. The polarographic current operates a galvanometer which controls the light reaching two photocells connected in opposition to the grid of a triode. A recording pen is operated by the output of the triode.

Fill and Stock (*21*) improved the Lingane-Kerlinger condenser circuit for damping current oscillations.

The construction of photographically recording polarographs based on the Heyrovský-Shikata principle has been described by Furman, Bricker, and Whitesell (*25*), Abichandani and Jatkar (*1*), and Lingane (*66*).

Philbrook and Grubb (*91*) described an improved wiring circuit for the Sargent-Heyrovský photographically recording polarograph, and a special vibration-free mounting for this instrument.

Modifications of the circuit of the Sargent-Heyrovský Model XI polarograph have also been described by Baumberger and Bardwell (*4*).

Caldwell and Reznek (*16*) devised a very simple manually operated circuit for polarographic measurements, which can be calibrated to read percentage directly.

The ingenious manually operated polarograph shown schematically in Figure 5, based on an original design by Breckpot of the University of Louvain, was described very recently by Favre (*20*).

Rotation of the hand wheel, *N*, increases the e.m.f. applied to the polarographic cell and simultaneously rotates the mirror, *M*. The galvanometer light spot, reflected from the mirror up to the large glass plate, *E*, moves along one axis in direct relation to the applied e.m.f. and along the other according to the current. A sheet of translucent graph paper is placed on the glass plate and as the hand wheel is rotated the path of the light spot is traced with a pencil to obtain the polarogram.

Although very simple, this instrument possesses many of the virtues of an automatic polarograph. A very similar *Handschreiber* incorporated in the older Leybold polarograph has been described by Hohn (*36*).

Two types of manual instruments for polarographic measurements developed recently at the Scientific Research Institute, Gor'kiĭ University, have been described by Korshunov and Rostokin (*50*).

Müller (*83*) has described simple polarographic instrumentation suitable for instructional purposes.

The writer has employed the simple manual circuit shown in Figure 6 for polarographic instruction in an advanced course in electroanalytical chemistry for several years.

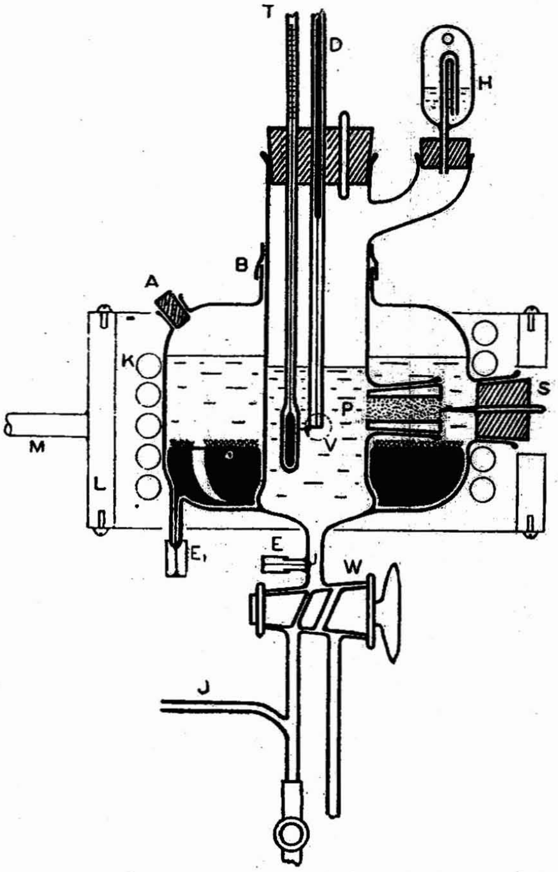

Figure 7. Thermostated Polarographic Cell Designed by Langer (*55*)

The polarographic bridge, R_1, is a 100-ohm radio type potentiometer (General Radio Co., Type 214) powered by two 1.5-volt dry cells. The current is measured in terms of the iR drop across the 10,000-ohm precision fixed resistance, R_2 (General Radio Co. Type 500-J). By reversing the double-pole double-throw switch the e.m.f. applied to the polarographic cell is measured with the same potentiometer used for the current measurement. Any ordinary potentiometer may be used. The galvanometer used with the potentiometer should be damped by a resistor across its terminals, so that the oscillations due to the growth and fall of the mercury drops at the dropping electrode do not extend over more than 1 or 2 cm. of the scale. The potentiometer is balanced so that the oscillations extend an equal distance on either side of the galvanometer zero point. Although very simple, this circuit provides polarographic measurements of higher accuracy than most commercial polarographs, and it is also very useful for amperometric titrations.

CELLS

The thermostated cell shown in Figure 7, with a capacity of 20 to 50 ml., was designed by Langer (*55*). The external calomel electrode is contained in the outer vessel and electrolytic connection is made through the porous ceramic plug, *P*. The two-way stopcock serves for the introduction of an inert gas through tube *J*, and for removal of the solution.

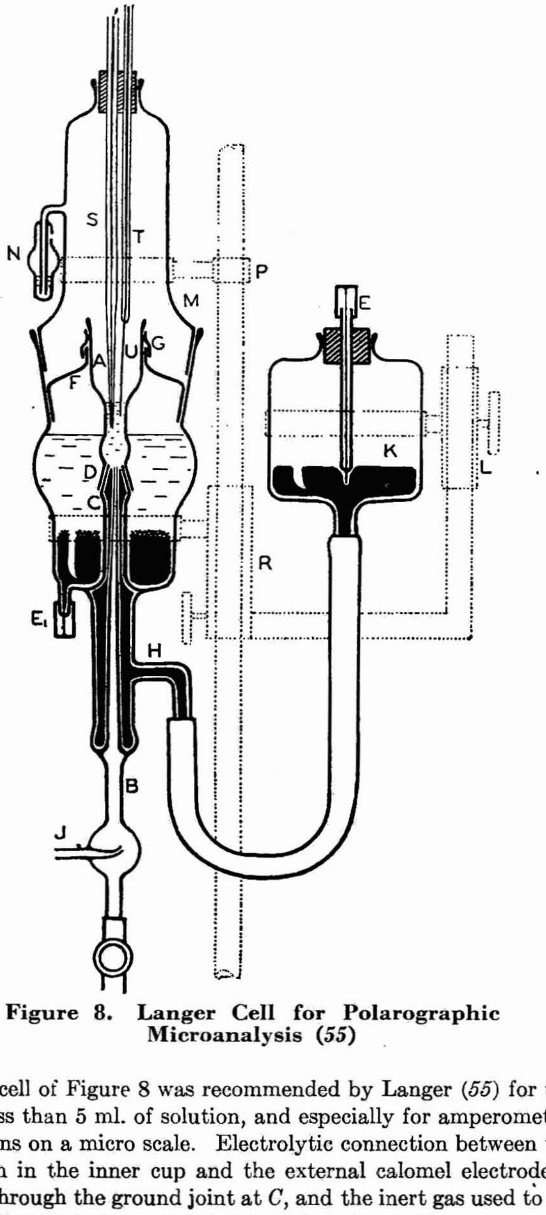

Figure 8. Langer Cell for Polarographic Microanalysis (*55*)

The cell of Figure 8 was recommended by Langer (*55*) for use with less than 5 ml. of solution, and especially for amperometric titrations on a micro scale. Electrolytic connection between the solution in the inner cup and the external calomel electrode is made through the ground joint at *C*, and the inert gas used to remove dissolved air is admitted by tubes *J* and *B*.

Beecher, Follansbee, Murphy, and Craig (*5*) modified the Lingane-Laitinen H-cell as shown in Figure 9, so that it could be used for determination of the oxygen content of 1-ml. samples of biological fluids. The chief problem was transfer of the sample to the cell without contact with air (or any gas phase) which would alter its oxygen content. This is effected by first raising mercury reservoir 1 until the cell is completely filled with mercury. The sample fluid (preserved under mineral oil) is then drawn into the cell through the capillary side tube and stopcock by lowering the mercury reservoir.

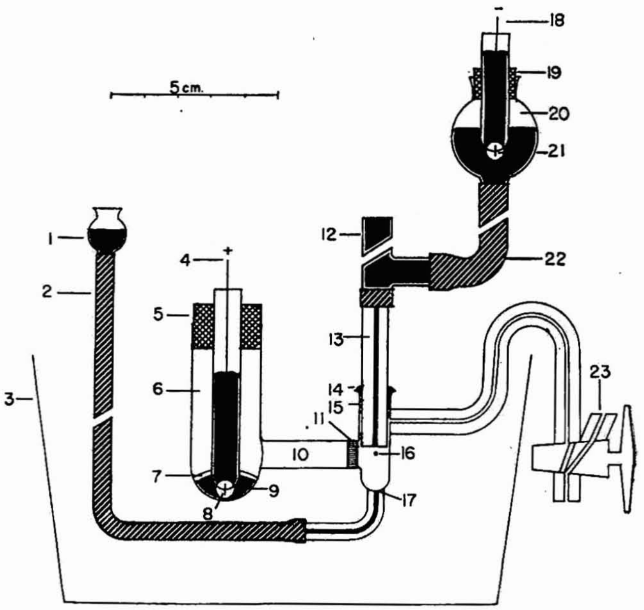

Figure 9. Beecher-Follansbee-Murphy-Craig Cell Especially Designed for Determination of Oxygen in Biological Fluids (*5*)

The cell in Figure 10 was designed by Lingane (*60*) for rapid routine analysis of 5 ml. volumes.

A silver wire wrapped around the end of the dropping electrode serves as a convenient anode, and its potential is stabilized by adding a small concentration of chloride ion (0.1 *N*) to the supporting electrolyte. The silver wire anode may be used with any supporting electrolyte in which silver chloride is insoluble (alkali and alkaline earth chlorides, tartrate and citrate solutions, sodium hydroxide, tetraalkylammonium halides and hydroxides, etc.), but it cannot be employed when the supporting electrolyte contains substances which form soluble complexes with silver ion (ammonia, cyanide media, etc.). A lead wire anode can be used in solutions, such as ammonia, in which the silver wire anode cannot be used. When the supporting electrolyte is alkaline sodium sulfite may be used instead of an inert gas to remove oxygen, and a small Erlenmeyer flask can then serve as a simple cell.

The rate of mercury flow from the dropping electrode is determined automatically to ±0.2% by the stop-clock circuit and the three tungsten contacts sealed into the upper part of the stand tube. To measure *m* the mercury reservoir is raised until the mercury level is slightly above the top contact. The screw clamp (or glass stopcock lubricated with Silicone lubricant) between the stand tube and mercury reservoir is then closed. When the mercury level falls below the top contact the short circuit around the clock is broken and the clock starts, and when the mercury level falls below the middle contact the clock stops. Thus the clock registers the time of flow of the weight of mercury equivalent to the volume between the two upper contacts. The contacts are placed so that this time is 10 to 15 minutes. The device measures the value of *m* corresponding to a mercury level exactly midway between the two upper contacts, and hence the mercury level is adjusted to this point during the polarographic measurements. This cell is especially convenient for routine polarographic analyses based on standardized diffusion current constants (*58*).

Lykken, Pompeo, and Weaver (*73*) recommended the "unitized" dropping electrode assembly shown in Figures 11 and 12 for routine use in a large industrial laboratory. The cell proper consists of a weighing bottle, and an internal pool of mercury is used as anode. The remainder of the assembly comprises a constant temperature bath, a holder for the dropping electrode which, together with the mercury reservoir, is held by a graduated steel rod, and apparatus for controlling the flow of inert gas used to remove dissolved air from the test solution.

Carritt (*18*) recommended the modified H-cell in Figure 13 to prevent chloride ion from the saturated calomel anode from contaminating the test solution.

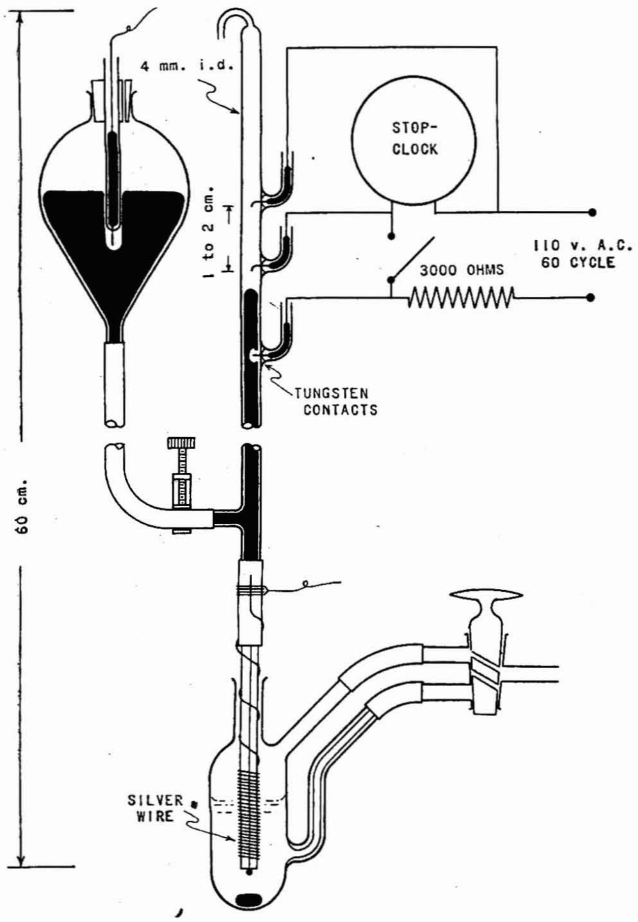

Figure 10. Lingane Cell for Rapid Routine Analysis

Based on standardized diffusion current constants, with silver wire anode and stop-clock circuit for automatic measurement of rate of flow of mercury (*60*)

The test solution is placed in the right-hand compartment and the inert gas is passed through the solution by way of the left-hand gas inlet tube and the inverted U connecting tube. When air has been removed the gas stream is passed over the surface of the solution by means of the right-hand gas inlet, and the connecting U-tube is then filled by applying gentle suction to the left-hand gas inlet tube. The long U-shaped connecting tube effectively prevents diffusion of chloride ion from the calomel electrode in the left-hand compartment into the test solution.

Baumberger and Bardwell (*4*) recommended the use of a hydrogen electrode as reference electrode in a polarographic cell. The potential of this reference electrode can be varied over a wide range by changing the pH of the buffer solution used.

Modifications of more or less conventional types of cells and dropping electrodes have been described by Gislard (*27*), Novak (*88*), West and Amis (*110*), Stock (*105*), Kanner and Coleman (*41*), Philbrook and Grubb (*91*), McReynolds (*76*), and Kahan (*39*).

SPECIAL MERCURY ELECTRODES

When diffusion is the controlling factor the current observed depends directly on the electrode area. With the dropping mercury electrode the average area during the drop life is directly proportional to the quantity $m^{2/3}t^{2/3}$, where m is the rate of mercury flow and t is the drop time. The average current is proportional to $m^{2/3}t^{1/6}$—i.e., to the average area divided by the square root of the drop time.

In order to increase the size (area) of the mercury drops Riches (*97*) suggested the use of a dropping electrode capillary with the radius at the orifice greater than the radius of the lumen higher in the tube. The electrode is constructed by sealing a very short length of relatively large capillary tubing to the bottom of a conventional dropping electrode capillary, and by proper choice of dimensions an electrode is obtained with a normal drop time (3 to 4 seconds) but a very large rate of flow of mercury (6 to 7 mg. sec.$^{-1}$). Because of the very large $m^{2/3}t^{1/6}$ factor (4 to 5 mg.$^{2/3}$ sec.$^{-1/2}$) the diffusion current measured with this type of electrode is much larger than with the conventional type. At first thought it might seem that the Riches electrode would result in

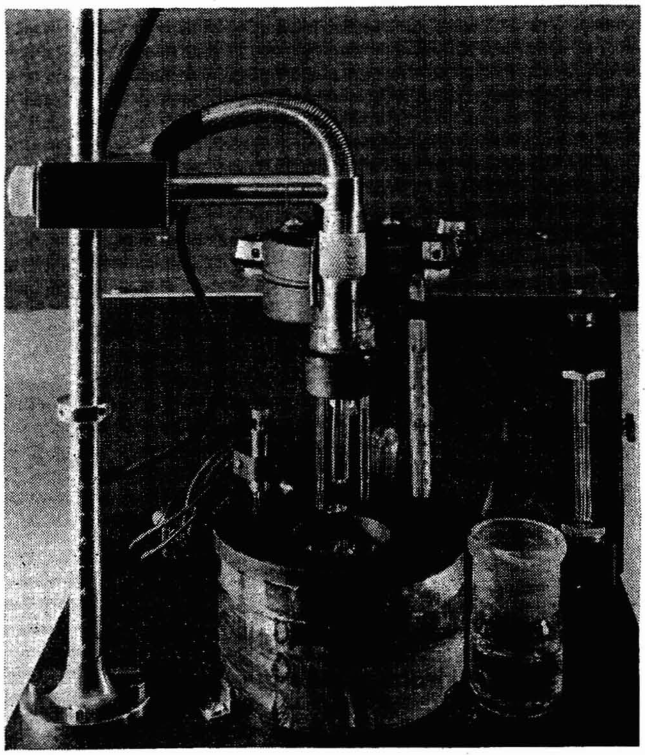

Figure 11. Lykken-Pompeo-Weaver Unitized Dropping Electrode Assembly (*73*)

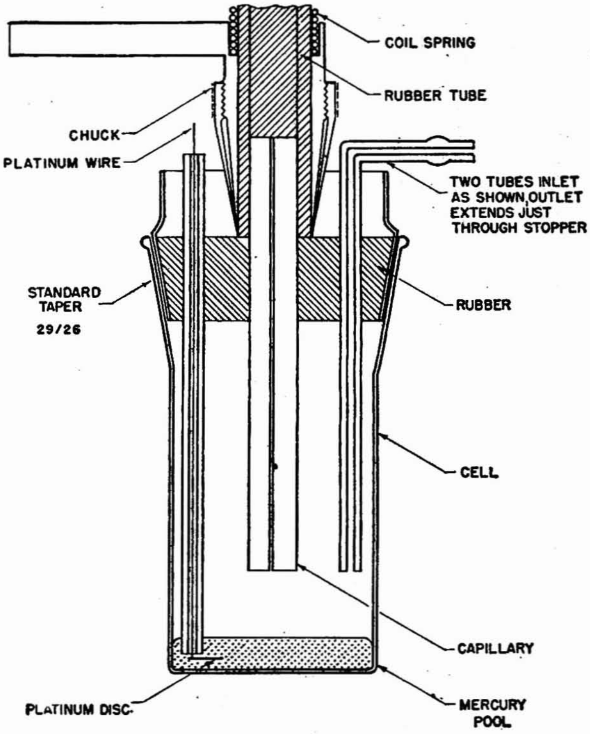

Figure 12. Lykken-Pompeo-Weaver Cell (*73*)

greater sensitivity, but actually this is not realized because the residual current, which also depends on the rate of flow of mercury, is increased correspondingly and there is little, if any, net gain.

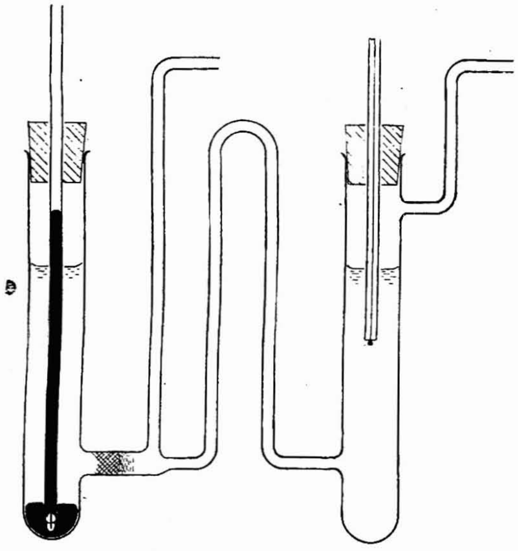

Figure 13. Carritt Modified H-Cell for Preventing Contamination of Test Solution by Constituents of Reference Electrode (*18*)

The use of a multiple-tip dropping electrode (four tips joined to a common tube) has been suggested by De Vries and Barnhart (*19*), as a means of increasing the diffusion current. From the Ilkovič equation the total current should obey the relation

$$i_d = 605\ nD^{1/2}C(m_1^{2/3}t_1^{1/6} + m_2^{2/3}t_2^{1/6} + \dots m_n^{2/3}t_n^{1/6})$$

and De Vries and Barnhart found that this was true with $n = 4$, and presumably with larger values. There is no appreciable gain in the real accuracy of determining small concentrations with multiple-tip electrodes because the residual current is increased in approximately the same proportion as the total current, and the real accuracy depends on the difference between the two. However, multiple-tip electrodes should be useful as a means of eliminating current oscillations in certain types of polarographic measurements. For this purpose it would be necessary to use a large number of tips (25 or more), so that the contribution of each electrode to the total would be small, and to ensure that the various mercury drops would always remain out of phase.

Multiple-tip dropping electrodes have also been discussed by Gilvery, Hawkings, and Thode (*26*).

To eliminate the effect of the periodic change in area of the classical type of dropping mercury electrode, Heyrovský and Forejt (*33*) invented the streaming mercury electrode shown in Figure 14. The mercury jet issuing upward from the capillary tube remains coherent while in the solution and thus constitutes a cylindrical electrode whose surface is continuously renewed but which retains a constant area defined by the size of the capillary orifice (ca. 0.1 mm.) and the distance between the capillary tip and the surface of the solution (4 to 8 mm.). The jet electrode is supplied with mercury at about 50-cm. pressure from the usual type of leveling bulb reservoir. This ingenious electrode was intended primarily for oscillographic studies, but it has interesting possibilities in practical polarographic analysis, if it can be designed so that its area is more exactly defined and more reproducible than the present form.

SOLID MICROELECTRODES

The apparent simplicity of solid metal microelectrodes is misleading, and their use usually poses more technical problems than the dropping mercury electrode. It is not easy to obtain reproducible currents with solid microelectrodes. This difficulty is due in part to less well defined diffusion conditions, which can be circumvented by employing rotating electrodes to define the diffusion layer more discretely, but a fundamental handicap is the fact that the current at any instant more often than not is found to depend on the pretreatment of the electrode, the previous history of the electrolysis, and similar factors. Solid metal microelectrodes are also severely limited in the direction of cathodic polarization by the relatively much lower potential at which hydrogen ion is reduced, compared to mercury electrodes. However, platinum microelectrodes potentially have a wider range of anodic application than the relatively easily oxidized mercury electrodes, and they are also more readily adaptable to automatic recording of diffusion currents over extended time intervals. Polarographic investigations with solid microelectrodes up to 1941 have been reviewed by Kolthoff and Lingane (*46*).

Miller (*78*) developed an ingenious method designed to overcome polarization difficulties with solid microelectrodes. The microelectrodes are platinum wires (bright or amalgamated) 0.5 to 6 mm. long and 0.1 to 0.5 mm. in diameter. The two electrodes are placed simultaneously in a solution, in conjunction with a large mercury or large platinum anode, and one of them is periodically employed as a polarized cathode while the other is "renewed" by being short-circuited to the large anode. A polarization period of 0.5 to 1 second is used. Miller claimed that this technique is suitable for the determination of metals less noble than mercury and for polarographic studies with fused electrolytes.

The use of solid electrodes (silver or amalgamated silver, gold, palladium, nickel, or copper) as polarographic anodes has been described by Sinyakova (*101*).

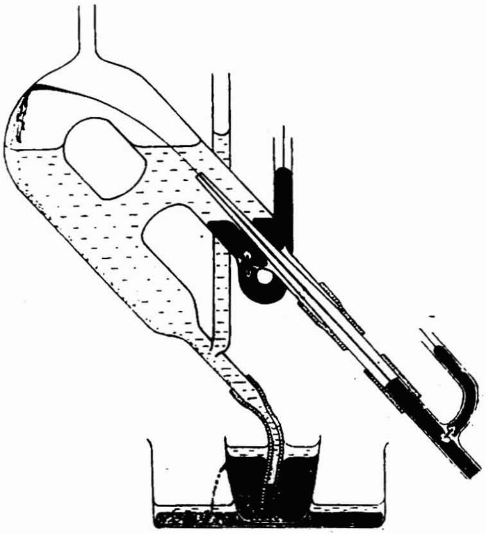

Figure 14. Heyrovský-Forejt Cell with Streaming Mercury Electrode (*33*)

Müller (*81*) has recently devised a new technique of polarographic measurement with a platinum microelectrode which involves flowing the solution past the electrode in a constricted glass tube. Under optimum conditions the limiting currents obtained were found to be a linear function of the concentration of the electroactive substance and the logarithm of the flow rate. Müller established the conditions that must be maintained to obtain reproducible results, and demonstrated the utility of the method for studying the reversibility of various electrode reactions.

The use of a Laitinen-Kolthoff type of rotating platinum microelectrode in place of the dropping electrode has been advocated by Morriss (*79*).

The automatic recording of polarograms with stationary and rotating platinum microelectrodes has been investigated anew by Skobets and Kacherova (*102*), who recommended such electrodes particularly for use in nonaqueous media and molten salts. A rotating electrode is much more amenable to automatic recording than a stationary electrode, because a relatively long time is required for the development of a steady state of diffusion and hence steady current with stationary electrodes in unstirred solutions. Consequently, automatically recorded curves with stationary electrodes show "time maxima" whose magnitudes depend on the rate of increase of the polarizing e.m.f., and reproducibility is difficult to attain.

THEORY

LIMITING CURRENTS CONTROLLED BY REACTION RATES

When two substances, A and B, are in chemical equilibrium with each other, and both are reducible but at different potentials, a polarogram of the solution will show the separate waves of each substance only under certain conditions.

Assuming that A is the more easily reducible, then at potentials corresponding to its limiting current the reaction $B \rightarrow A$ will proceed to a greater or lesser degree at the electrode surface as A is removed by reduction, and the additional A thus formed is immediately reduced. If the rate of conversion of B to A is very great, complete transformation will occur and only a single wave will appear on the polarogram. The potential of this wave will correspond to the reduction potential of A. With smaller values of the rate constant of the $B \rightarrow A$ reaction, separate waves due to reduction of A and B can appear.

If the rate of attainment of equilibrium is exceedingly slow, the relative heights of the two waves will be governed solely by the rates of diffusion of A and B and their ratio will obey the equation

$$\frac{i_A}{i_B} = \frac{n_A D_A^{1/2} C_A}{n_B D_B^{1/2} C_B} \qquad (1)$$

where n is the number of electrons transferred per molecule reduced, and D and C are, respectively, the diffusion coefficient and equilibrium concentration of each species.

With intermediate values of the rate constant for $B \rightarrow A$, the relative wave heights will not be proportional to the relative equilibrium concentrations of A and B, but the wave of A will be relatively larger, and the wave of B will be proportionally smaller, to a degree dependent on the magnitude of the rate constant. The excess height of wave A also depends on the drop time, since the latter determines the total amount of conversion of B to A that occurs, and it is to be expected that the relative height of wave A will increase with increasing drop time.

These phenomena have been observed with various types of equilibria, one of the best known being mixtures of certain reducible acids and their anions. Furman and Bricker (*23*) in their study of *o*-phthalic acid were among the first to recognize the fact that the anion of a weak acid may be reduced at a more negative potential than the undissociated acid, and that two waves appear over a certain pH range that lies at or above the value of pK for the acid. Furman and Bricker demonstrated that the curve showing the relative height of the first wave as a function of pH virtually overlapped the curve for the relative equilibrium concentration of phthalic acid. The fact that the curves span nearly identical pH ranges shows that the rate of the association reaction

$$A^- + H^+ = HA \qquad (2)$$

is in this particular case very slow, and the relative wave heights thus correspond closely to the relative equilibrium concentrations of phthalic acid and hydrogen phthalate ion.

Important progress in the direction of a quantitative interpretation of "rate currents" has recently been made by Brdicka, Wiesner, and their colleagues at Prague (*9, 10, 51*). Brdicka demonstrated that the double waves observed over limited pH ranges with pyruvic and phenylglyoxylic acids result from reduction of the undissociated acids and their anions, the free acid being the more easily reducible in each case. The double waves of pyruvic acid were first investigated systematically by Müller and Baumberger (*84*) who attributed them to keto-enol tautomerism, but Brdicka has presented evidence which disproves this interpretation.

Although the dissociation constant of phenylglyoxylic acid is 6.4×10^{-2} (pK = 1.2), only the first wave corresponding to the reduction of HA is observed up to a pH of about 5. This shows that in this case the rate of association according to Equation 2 proceeds rapidly enough to replenish HA at the electrode surface as fast as it is removed by reduction. At pH above 5 the equilibrium concentration of HA becomes infinitesimal, the association reaction is unable to maintain equilibrium, and consequently the second wave due to reduction of A^- appears. The first wave does not entirely disappear until the pH exceeds about 8, at which point the equilibrium proportion of undissociated phenylglyoxylic acid is only about 10^{-7}. At pH values above about 3 the limiting current of the first wave is virtually a pure rate current. The total height of both waves is practically constant and independent of pH.

Brdicka showed that the relative separate heights of the two waves as a function of pH obeyed the relation

$$\text{pH} = \text{constant} + \log \frac{i_2}{i_1} \qquad (3)$$

where the constant depends on both pK and the rate constant of Reaction 2, and has a value of approximately 5.6 in the case of phenylglyoxylic acid and about 3.8 in the case of pyruvic acid.

Brdicka and Wiesner (*10*) assumed that the limiting current of the first wave was the sum of a contribution by diffusion of HA molecules from the body of the solution, and a kinetic current, i_k, proportional to $kC_A^0C_H^0$, where k is the rate constant of the association reaction and C_A^0 and C_H^0 are the concentrations of A^- and H^+ at the electrode surface. In well buffered solutions the concentration of hydrogen ion at the electrode surface does not differ materially from its value in the body of the solution. On this basis the kinetic current was expressed as

$$i_k = nFqukC_HC_A^0 \qquad (4)$$

where q is the area of the mercury drops and u the thickness of the layer in which the association reaction occurs. Brdicka and Wiesner further assumed that the kinetic current was related to the concentration of A^- in the body of the solution, C_A, and that at the electrode surface by

$$i_k = \alpha\,(C_A - C_A^0) \qquad (5)$$

where the proportionality constant α is defined by the Ilkovič equation, and is equal to $605\, nD_A^{1/2}m^{2/3}t^{1/6}$ when the usual units are employed. They then combined these two equations, expressed C_A in terms of the dissociation constant of the acid and the total concentration C of HA and A^- in the solution, and arrived at the following equation for the kinetic current

$$i_k = \frac{\alpha\, ukKCC_H}{(K + C_H)\left[ukC_H + \dfrac{\alpha}{nFq}\right]} \qquad (6)$$

In order to obtain an equation for the total limiting current of the first wave, i_1, Brdicka and Wiesner postulated

$$i_1 = i_d + i_k \qquad (7)$$

where the diffusion component of the current is assumed to obey the Ilkovič equation. They also assumed that the diffusion coefficients of HA and A^- are equal, and finally arrived at the relation

$$i_1 = \frac{\alpha CC_H}{(K + C_H)}\left[\frac{uk\,(K + C_H) + \dfrac{\alpha}{nFq}}{ukC_H + \dfrac{\alpha}{nFq}}\right] \qquad (8)$$

Equation 8 is consistent with the fact that when k is extremely large i_1 is independent of pH over a rather wide range and is governed only by the total concentration, C, of HA and A^-—i.e., the second wave is absent. When k is virtually zero the entire bracketed term becomes equal to 1, and i_1 then corresponds to the ordinary diffusion current of HA proportional to C_{HA} in the body of the solution.

Because of the unknown and rather fictitious quantity u, it is not possible to compute k unequivocally from the observed values of i_l. Brdicka and Wiesner assumed that u was of the order of 10^{-7} cm. but this has little justification. The assumption that the diffusion component of the total limiting current obeys the Ilkovič equation is also highly uncertain, because when the association reaction is operative the concentration gradient of HA in the diffusion layer must be considerably altered and will not conform to the conditions assumed in the derivation of the Ilkovič equation. The same serious uncertainty applies to the diffusion of A^-, and hence the validity of equation 5 is questionable.

Recognizing some of the uncertainties in the foregoing derivation, Koutecky and Brdicka (*51*) later presented a more rigorous theoretical development of equations for the kinetic current. Among other refinements they took account of the probability that the association reaction can involve other proton donors than the hydronium ion. It is not possible in the space available here to do justice to the 12-page mathematical treatment of Kautecky and Brdicka, nor even adequately to interpret the complex final equations which they produced, and the reader is urged to consult the original paper.

Brdicka (*9*) showed that at a pH of 8 the first wave of phenylglyoxylic acid remains virtually constant as the drop time is increased by decreasing the pressure on the dropping mercury, but the total height of both waves shows the expected normal decrease. In other words, the relative height of the first wave increases with increasing drop time. This reflects the fact that the kinetic current is proportional to the average area of the mercury drops—i.e., to $m^{2/3}t^{2/3}$—and it is well known that the average area of the drops is almost independent of the pressure on the dropping electrode. This behavior is a generally useful criterion of a rate-controlled limiting current.

The principles underlying the polarographic investigation of tautomeric equilibria have also been discussed by Brdicka (*9*).

The reduction wave observed with solutions of certain sugars is another example of a rate-controlled limiting current. In an early study Cantor and Peniston (*17*) concluded that the height of the single wave corresponded to the equilibrium concentration of the reducible aldehydo form of the sugar. Very recently Wiesner (*111*) showed that the equilibrium concentrations of the reducible forms of glucose, galactose, and xylose under the conditions employed are much too small to produce a detectable wave, and that the wave observed actually results from the rate-controlled production of the reducible form at the electrode surface.

Vesely and Brdicka (*109*) recently demonstrated that the limiting current observed in the reduction of formaldehyde can be interpreted as a kinetic current, governed by the dehydration rate of hydrated formaldehyde molecules at the surface of the dropping electrode. They studied the effect of acid-base catalysis, and were able to explain satisfactorily the anomalous behavior of the limiting current with changes in pH and temperature. Bieber and Trümpler (*6*) have presented a similar interpretation.

The first of the two waves observed with phenylnitrosohydroxylamine (cupferron) in solutions of pH between 7 and 9 was shown by Kolthoff and Liberti (*45*) to include a kinetic current due to the association of the anion form of the substance with hydrogen ion to produce the more easily reducible acid form at the electrode surface.

The "catalytic waves" observed with various substances are further instances of limiting currents controlled by reaction rates. Recent pertinent studies include the work of Brdicka and Wiesner (*11*) on the catalyzed reduction of hydrogen peroxide, the investigation by Wiesner (*112*) of the oxidation of the reduced forms of various dyestuffs at the dropping electrode catalyzed by a hydrogen-saturated suspension of palladium, and the catalytic reduction of hydrogen ion by various substances.

DIFFUSION CURRENT

Influence of Capillary Characteristics. The fundamental equation for the diffusion current with the dropping mercury electrode, first derived by Ilkovič, is

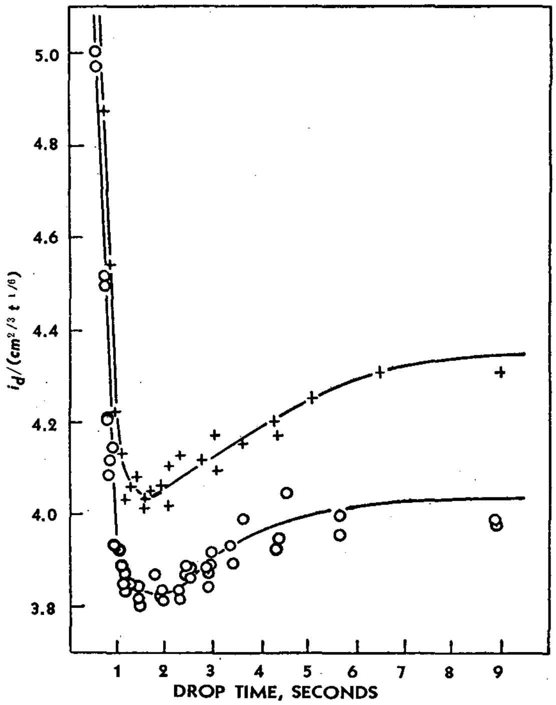

Figure 15. Influence of Capillary Characteristics on Diffusion Current Constant (*67*)

Upper curve obtained with tetrammino zinc ion and lower curve with lead ion

$$i_d = 605\ nD^{1/2}Cm^{2/3}t^{1/6} \tag{9}$$

where n is the number of electron equivalents per molar unit of the electrode reaction, D is the diffusion coefficient (cm.² sec.$^{-1}$) of the reducible or oxidizable substance, C is its concentration (millimoles per liter), m is the rate of flow of mercury (mg. sec.$^{-1}$), t is the drop time (seconds), and the constant 605 is a combination of universal and geometrical constants. Studies of this relation up to 1941, which have established its essential validity, have been discussed in detail by Kolthoff and Lingane (*46*).

Lingane and Loveridge (*67*) recently tested the predicted linear relation between i_d and $m^{2/3}t^{1/6}$ with capillaries covering a range of m-values from 0.9 to 16 mg. sec.$^{-1}$ and a range of drop times from 0.5 to 9 seconds. Measurements were made with lead ion in 1 M potassium chloride and with zinc ion in 1 M ammonium chloride—1 M ammonia, with 0.01% gelatin as a maximum suppressor in both cases. Three different measurement techniques were employed, every known precaution was taken to minimize experimental errors, and a precision (reproducibility) of about ±0.5% was attained. The results obtained are summarized graphically in Figure 15, in which the quantity $i_d/(Cm^{2/3}t^{1/6})$ is plotted against drop time. If the Ilkovič equation were strictly obeyed, this plot should simply be a horizontal straight line.

Curves of the same general shape as those in Figure 15 were also obtained by Buckley and Taylor (*13*) with several different metal ions. Their curves do not show minima, because the measurements were not sufficiently precise, but they do display the same very rapid increase of $i_d/(Cm^{2/3}t^{1/6})$ at small drop times. Buckley and Taylor found that gelatin, and presumably other maximum suppressors, has a very pronounced influence on the critical drop time below which the Ilkovič equation fails. Without gelatin failure occurred even with drop times as large as 3 to 4 seconds, and as gelatin was added in amounts up to about 0.008% the critical drop time decreased to the neighborhood of 1.5 seconds. According to Buckley and Taylor, the critical drop time for a given gelatin concentration is independent of the nature of the reducible ion, its concentration, and the supporting electrolyte.

The very rapid increase in $i_d/(Cm^{2/3}t^{1/6})$ at drop times smaller than about 1.5 seconds is doubtless caused by the stirring produced by the rapidly forming drops, with consequent disturbance of the diffusion layer. The increase of $i_d/(Cm^{2/3}t^{1/6})$ with increasing drop time above 1.5 seconds points to a real failure of the Ilkovič equation. The variation of $i_d/(Cm^{2/3}t^{1/6})$ is small enough over the 3- to 6-second range of drop times normally used not to invalidate the use of the Ilkovič equation in practical polarographic analysis. The use of very short droptimes has occasionally been recommended as a means of minimizing the current oscillations, and the curves in Figure 15 show that very serious errors can arise when this practice is followed.

The small variation of $i_d/(Cm^{2/3}t^{1/6})$ at drop times above 1.5 seconds indicates that the conditions actually extant differ significantly from those assumed in the derivation of the Ilkovič equation. One of the important assumptions is that the mercury drops are true spheres, but cinematic photographs taken by MacNevin and Balis (*75*) show that, although this is very nearly true, there is an appreciable elongation or tear shape during the latter stages of the drop life. Furthermore, because of the finite cross-sectional area of the lumen of the capillary the area is not exactly zero at zero time, and in addition the area of the small "neck" from which the drop is suspended may not be negligible. The fact that when each new drop begins to form the solution around it is still in motion as a result of the fall of the preceding drop is an additional complicating influence. As a result of these several factors one may expect that the current-time curve during the drop life will differ significantly from the pure sixth-order parabola predicated in the derivation of the Ilkovič equation.

In private conversation with the writer H. A. McKenzie of the Australian Scientific Office described experiments with a very rapid recorder which indicate that the current during the initial stages of drop formation is smaller than expected for a sixth-order parabola, and during the remainder of the drop life the current increases more nearly with the one-third than the one-sixth power of the time. A small but reproducible discontinuity in the current-time curve also appeared after about the first 10% of the drop life. It is to be expected that a closer approach to the ideal current-time curve will result the longer the drop time. These observations may provide the key to the explanation of the shape of the right-hand branch of the curves in Figure 15.

As a result of compensating factors the current-time curves of individual drops can vary significantly from the ideal sixth-order parabola without greatly changing the exponent of t with respect to the average current during the drop life to which the Ilkovič equation pertains. That the exponent of t for the average current is at least close to $^1/_6$ is conclusively proved by the fact that i_d is a linear function of the square root of the height of the mercury reservoir as demanded by $t^{1/6}$, whereas if the exponent were, say, $^1/_3$, the average diffusion current would depend on the cube root of the applied pressure. Data presented by Lingane and Loveridge (*67*) demonstrate that the square root relation is valid to about $\pm 1\%$ over a rather wide range of pressure, provided proper correction is made for the back pressure caused by the interfacial tension.

The final conclusion from these results is that the expected linear relation between i_d and $m^{2/3}t^{1/6}$ is obeyed to about $\pm 2\%$, provided the drop time is greater than about 2 seconds and 0.005 to 0.01% gelatin is present as a maximum suppressor.

The influence of the potential, rate of dropping, capillary dimensions, and concentration of supporting electrolyte on the tangential movement of solution around the dropping electrode was studied by Kryukova and Kabanov (*52*). Agar (*2*) and Levich (*56*) have recently presented theories of diffusion and convection at electrodes which have a direct bearing on the interpretation of polarographic limiting currents.

Loveridge (*72*) systematically investigated the influence of various factors on m and t. He found that the m-value in air is significantly larger than in aqueous solutions, because of the different back pressure resulting from the interfacial tension at the mercury surface, the difference varying from 0.5 to 3.5%. Hence in exacting work m must be measured in the supporting electrolyte used, rather than in air. Kolthoff and Kahan (*44*) observed that the mercury drops forming in air or in pure water tend to adhere to the glass surrounding the capillary orifice.

The influence on the diffusion current of tilting the dropping electrode from a vertical position was studied by Loveridge (*72*), who found that an inclination up to about 5° has no appreciable influence but that larger degrees of tilt cause the diffusion current to decrease and become less reproducible.

Müller (*80*) has called attention to the fact that irregular drop formation ensues when the flat end of the capillary is not horizontal. He has also described methods for determining the radius of the capillary by the critical pressure at which flow of mercury ceases, and also by the classical drop weight technique.

Diffusion Current as Function of Viscosity. For diffusing particles that are large compared to the solvent molecules the Stokes-Einstein relation predicts that the diffusion coefficient D should be inversely proportional to the viscosity coefficient η of the medium (*46*). Because the diffusion current depends on $D^{1/2}$ the relation $i_d = k/\eta^{1/2}$ should be obeyed under the conditions for which the Stokes-Einstein relation is valid.

Brasher and Jones (*8*) found that the diffusion currents of various metal ions in supporting electrolytes composed of 0.01 to 9 M sulfuric acid, 0.1 to 7 M sodium hydroxide, and 0.05 to 1 M sodium sulfate were inversely proportional to $\eta^{1/2}$ in agreement with the foregoing relation.

D. E. Carritt and the writer also observed that the product $i_d\eta^{1/2}$ remains very nearly constant in the reduction of +6 molybdenum from various concentrations of sulfuric acid between 0.2 and 12 M.

Contrariwise, Vavruch (*108*) claimed that the simple relation $i_d = k/\eta^{1/2}$ is not obeyed in the reduction of various metal ions in 0.1 M solutions of sodium chloride, sodium nitrate, and potassium sulfate when the viscosity is increased by addition of up to 50% saccharose. He concluded that the product $i_d\eta^{1/2}$ increased significantly with increasing viscosity.

McKenzie (*74*) has not been able to confirm Vavruch's conclusion, and has found that the diffusion currents of lead, cadmium, zinc, ascorbic acid, maleic acid, and Orange II, do follow the relation $i_d \doteq k/\eta^{1/2}$ in various concentrations of sucrose up to 43% (relative viscosity 4.86). McKenzie also observed that changes in viscosity produced by lyophilic colloids (gelatin, pectin, methylcellulose) have a much smaller influence on the diffusion current than the foregoing relation predicts. It appears that the product $i_d\eta^{1/2}$ does remain nearly constant when the viscosity is altered by changing the concentrations of substances in true solution, but when the viscosity is governed by a lyophilic colloid the product $i_d\eta^{1/2}$ increases with increasing η.

Hydrolysis Current of Metal Ions. In unbuffered solutions of certain metal salts the hydrogen ion produced by hydrolysis of the metal ion contributes to the total diffusion current at potentials more negative than the reduction potential of hydrogen ion. For example, polarograms obtained with chromic salts in unbuffered supporting electrolytes show two reduction waves, the first of which results from $Cr^{+++} + e = Cr^{++}$ and the second from $Cr^{+++} + 3e = Cr$, but the total height of both waves is considerably larger than three times the height of the first because of the simultaneous reduction of the hydrogen ion produced by hydrolysis of the chromic ion

$$Cr(H_2O)_6^{+++} = Cr(OH)(H_2O)_5^{++} + H^+ \qquad (10)$$

Lingane and Pecsok (*70*) recently demonstrated that this "hydrolysis current" can be interpreted quantitatively by the equation

$$i_H = 605\,(D_H^{1/2} - D_{Cr}^{1/2})C_H m^{2/3}t^{1/6} \qquad (11)$$

or the equivalent relation

$$i_H = (I_H - I_{Cr})C_H m^{2/3}t^{1/6} \qquad (12)$$

where D_H and D_{Cr} are the diffusion coefficients of hydrogen ion and hydrolyzed chromic ion, respectively, I_H and I_{Cr} are the corresponding diffusion current constants (605 $D^{1/2}$), and C_H is the equilibrium concentration of hydrogen ion in the body of the hydrolyzed solution. As the concentrations of hydrogen ion and hydrolyzed chromic ion are equal in the body of the solution, and the hydrogen ion which diffuses up to the surface of the dropping electrode is neutralized by the hydroxyl ion liberated at the electrode by the reduction of the hydrolyzed chromic ion

$$Cr(OH)(H_2O)_5^{++} + 3e = Cr + 5H_2O + OH^- \qquad (13)$$

as well as by the reversal of the hydrolytic equilibrium 10 in the diffusion layer, there would be no contribution at all of hydrogen ion to the total diffusion current if D_{Cr} were equal to D_H. The observed hydrolysis current results from the fact that the diffusion coefficient of hydrogen ion actually is much larger than that of the hydrolyzed chromic ion.

Since the degree of hydrolysis increases with increasing dilution, the relative value of i_H increases with decreasing concentration of the chromic salt. Consequently, a nonlinear dependence of total diffusion current on concentration results with unbuffered solutions of hydrolyzable metal ions, when the current is measured at potentials more negative than the reduction potential of hydrogen ion, and hence buffered solutions should be employed in practical determinations of such metals.

WATER CURRENT

Orlemann and Kolthoff (*49, 89*) discovered that under certain conditions an anomalous current is observed with the dropping electrode at potentials more negative than −0.9 volt versus the saturated calomel electrode. They attributed this current to the direct combination of water molecules and electrons, $H_2O + e \longrightarrow {}^1/_2 H_2 + OH^-$, and presented cogent evidence in support of this conclusion. That the "water current" is not due merely to some sort of stirring at the electrode surface was established by experiments which showed that hydroxide ion is formed at the surface of the mercury drops when the anomalous current is observed. They showed that the water current is observed only when the concentration of the supporting electrolyte is greater than about 0.5 *M*, and when a current due to the reduction of some other substance is flowing. Addition of small amounts of gelatin, and other substances which are strongly adsorbed on the dropping mercury electrode, eliminates the water current. It was also found that the water current is not obtained with a small stationary mercury electrode, from which Orlemann and Kolthoff concluded that water molecules are brought into an adsorbed layer at the electrode surface only during the establishment of the double layer and hence only when the electrode area is continuously increasing. This interpretation assumes that water molecules are reducible in virtue of the polarization which they undergo when they are present in an adsorbed layer at the electrode surface.

Orlemann and Kolthoff found that the water current, i_{H_2O}, was related to the total current, i, and to the characteristics of the dropping electrode capillary by the equation $i_{H_2O} = ki/m^{1/3}t^{4/3}$.

SIMULTANEOUS CATHODIC-ANODIC REACTIONS

Polarography has produced many electrochemical oddities, among which is the apparent paradox that a cathodic (reduction) reaction involving one substance can occur simultaneously with an anodic (oxidation) reaction involving another, the net diffusion current being the difference between the separate diffusion currents of the two substances. This phenomenon was originally recognized by Kolthoff and Miller (*47*), who observed that the reduction of oxygen in alkaline medium, $O_2 + 2H_2O + 2e = H_2O_2 + 2OH^-$, to produce a cathodic diffusion current proceeds independently of the depolarization of the dropping electrode by sulfide ion, $Hg + S^{--} = HgS + 2e$, which produces an anodic current. Hence over the range of potentials between the half-wave potentials of the two reactions the net current is the difference between the two.

The polarograms in Figure 16 (*64*) demonstrate another example of this behavior.

The polarograms were recorded with a solution of stannous tin in a weakly acidic tartrate supporting electrolyte (pH = 4.3) to which increasing amounts of copper were added. In this medium the reduction of the cupric tartrate complex produces a cathodic wave at −0.09 volt versus the saturated calomel electrode, and the half-wave potential of the anodic wave resulting from the oxidation of the stannous tartrate complex has the more negative value −0.28 volt. At potentials between these values both reactions occur simultaneously and independently. The cathodic wave of relatively small amounts of copper is manifested on the anodic part of the polarogram (*a* to *b*), and when an excess of copper is present the anodic stannous wave becomes a part of the cathodic portion of the polarogram (*b* to *c*).

The net current measured between the two half-wave potentials—i.e., at −0.2 volt—becomes zero when the flux of copper is equal to the flux of the stannous tin at the electrode surface, and this condition is realized when the $CD^{1/2}$ products for each of the two are equal. It is thus possible to perform an amperometric titration of stannous tin with cupric ion, although there is actually no appreciable direct reaction between the two in the body of the solution. The cathodic wave at −0.6 volt is due to the reduction of the stannous tartrate complex to the metal.

Simultaneous cathodic-anodic currents are possible, of course, only when the thermodynamic condition for a direct chemical reaction is satisfied, as otherwise overlapping waves would be impossible. The fact that current compensation occurs without direct reaction merely shows that the rate of the direct reaction is very small compared to the rates of the individual electrode reactions.

MUTUALLY INTERFERING REDUCTION REACTIONS

In the great majority of cases various reducible substances in a mixture produce their individual polarographic waves and dif-

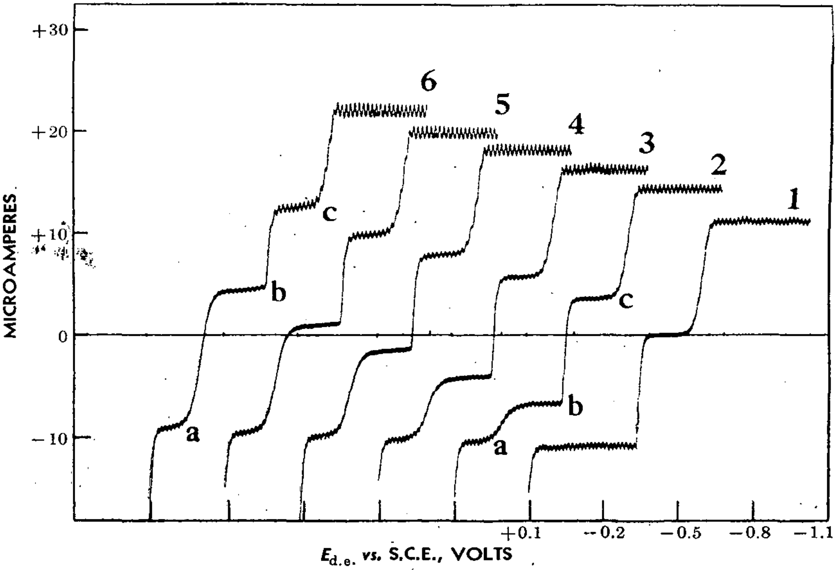

Figure 16. Polarograms of Mixtures of +2 Copper and +2 Tin in Acidic Tartrate Supporting Electrolyte, Demonstrating Simultaneous Cathodic and Anodic Reactions (*64*)

Curve 1 recorded with 2 millimolar stannous tin alone, and others after addition of increasing amounts of copper

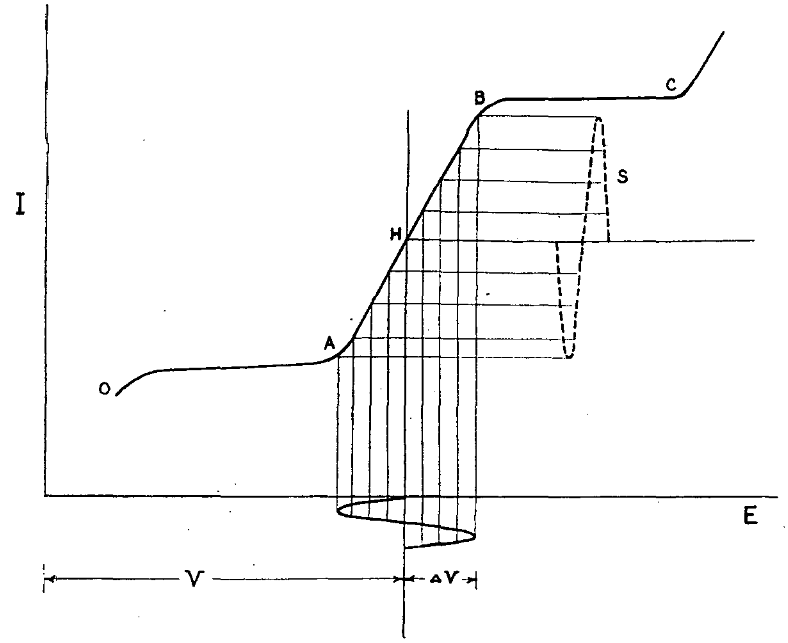

Figure 17. Principle of Müller-Garman-Droz-Petras Oscilloscopic Technique (*86*)

fusion currents exactly as in their single solutions without interfering with each other. If this were not true practical polarographic analysis could not exist. Some interesting instances of mutual interferences are known, however; one of the first observed was the diminution of the diffusion current of hydrogen ion by its reaction with the hydroxide ion produced by the simultaneous reduction of oxygen in unbuffered solutions, as reported by Kolthoff and Miller (*48*).

Other examples of anomalous wave heights produced by chemical reaction of the reduction product of one substance with the oxidized form of another have been observed by Lingane and Niedrach (*69*) with mixtures of selenium or tellurium with other metals.

Polarograms of mixtures of +4 selenium and copper in ammoniacal medium show well developed waves for both elements, the double copper wave preceding that of selenium by nearly 1 volt, but the height of the selenium wave is much smaller than in the absence of copper. This is caused not by a decrease of the diffusion current of the selenium, but by the fact that the selenide ion produced at the electrode surface by the reduction of the +4 selenium, $SeO_3^{--} + 6H^+ + 6e = S^{--} + 3H_2O$, reacts with the incoming cupric ammonia complex in the diffusion layer to precipitate cupric selenide, $Cu(NH_3)_4^{++} + Se^{--} = CuSe + 4NH_3$. Consequently, the contribution of the copper to the total diffusion current is diminished at potentials at which the selenium is reduced. The total diffusion current remains unchanged as copper is added until the product $CD^{1/2}$ for the copper is equal to the same product for the selenium, and then increases in direct proportion to the copper added in excess.

The same effect was observed (*69*) with alkaline solutions of +4 tellurium to which lead ion or cupric ion was added.

It should be possible to utilize this phenomenon for the amperometric titration of selenium and tellurium.

POLAROGRAPHY IN LIQUID AMMONIA

The polarographic behavior of the alkali metals in anhydrous liquid ammonia at −36° C. was described recently by Laitinen and Nyman (*54*). All five of the alkali metals were found to undergo nearly reversible reduction. The half-wave potentials shifted regularly to more positive values in going from lithium to cesium, and were in good agreement with theoretical values. The diffusion currents were linear functions of concentration, and the observed values agreed reasonably well with the values predicted by the Ilkovič equation.

POLAROGRAPHY IN FUSED SALT MEDIA

Nachtrieb and Steinberg (*87*) have reported briefly on polarographic experiments in anhydrous fused salt media.

A ternary eutectic consisting of 66.65 mole % ammonium nitrate, 25.76% lithium nitrate, and 7.59% ammonium chloride (melting point 86.2° C.) was used at a temperature of 125° C. An ordinary dropping mercury electrode in conjunction with a mercury pool anode was used. Normal reduction waves were obtained with nickel (II), copper (II), and bismuth (III). Data presented demonstrate that the Ilkovič equation is obeyed in this medium, and in the case of nickel the diffusion current constant $i_d/(Cm^{2/3}t^{1/6})$ was found to be 1.18 ± 0.05 over the concentration range 2 to 12 millimolar. This is about one third as large as the diffusion current constant of nickelous ion in aqueous solutions at room temperature, the difference doubtless being due to the relatively greater viscosity of the fused salt medium.

METHODOLOGY

Important factors that must be considered in quantitative polarographic analysis have been reviewed by Kolthoff and Lingane (*46*), Kolthoff (*43*), Heyrovský (*32*), Buckley and Taylor (*14*), and Müller (*82, 83*).

OSCILLOSCOPIC POLAROGRAPHY

Müller, Garman, Droz, and Petras (*86*) were among the first to apply the cathode ray oscilloscope to polarographic measurements.

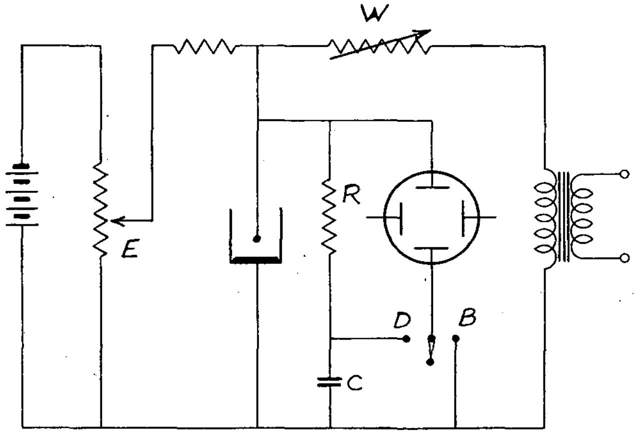

Figure 18. Oscilloscopic Circuit of Heyrovský and Forejt (*33*)

The principle of their technique is indicated in Figure 17, where *OAHBC* represents the ordinary polarographic wave. Provision is made (*86*) for polarizing the dropping electrode with direct current in the ordinary way, and a small and adjustable sinusoidal alternating voltage is also superimposed on the cell. The magnitude of the superimposed alternating voltage is adjusted to correspond to the width of the wave as indicated in Figure 17. The alternating current component is applied to the vertical deflecting plates of a high gain (3000 to 5000 ×) oscilloscope via a low primary impedance, high gain transformer. The sweep frequency is synchronized with the 60-cycle applied alternating current to produce a Lissajous pattern whose vertical component corresponds only to the alternating current through the cell, the vertical amplitude being proportional to the slope of the polarographic wave. An ordinary dropping electrode is used. When the applied direct current voltage is adjusted exactly to the half-wave potential H, a perfectly symmetrical sinusoidal figure S appears, as shown in Figure 17, but very small displacements of the direct current voltage above or below the half-wave potential produce relatively large distortions of the figure.

The circuit is particularly useful for precise and rapid determinations of the reduction potentials of various substances in mixtures, and with refinements it should also be possible to employ it for quantitative purposes, as with all other conditions constant the vertical dimension of the Lissajous figure is a function of the magnitude of the diffusion current and hence concentration.

Matheson and Nichols (*77*) independently developed a different oscillographic technique based on the application of a linear voltage sweep (30 cycles, 0–2.4–0 volts) to the dropping electrode. The resulting current is measured by placing a known resistance in series with the cell and applying the iR drop developed across it to the vertical plates of the oscilloscope. The resulting Lissajous figure is a nearly instantaneous current—voltage curve whose shape corresponds closely to polarograms obtained in the classical manner. With the usual drop time of about 3 seconds, the figure grows vertically during the drop life as a consequence of the increasing electrode area. This can be eliminated, and a stationary figure obtained, by synchronizing the voltage sweep and drop time (*77*). Such synchronization is difficult to achieve and maintain and with the very rapid dropping rate required the Ilkovič equation will no longer apply. The relatively tremendous charging current produced by the rapid voltage sweep further complicates quantitative measurements.

The circuit is most useful for investigating the rates and reversibility of reactions at the dropping electrode. For example, the Lissajous pattern observed by Matheson and Nichols with manganous ion in 0.1 M lithium chloride shows a more or less normal cathodic wave, but no anodic wave appears in the trace during the return voltage sweep. Evidently the reaction $\mathrm{Mn}^{++} + 2e = \mathrm{Mn}$ does not proceed reversibly, the overvoltage involved in the reverse (oxidation) direction being much larger than the cathodic overvoltage.

Boeke and van Suchtelen (*7*) described an oscillographic technique based on the simultaneous application of alternating and direct current voltage to a polarographic cell as in the method of Müller *et al.*, but employing the phase shift between current and voltage above and below the half-wave potential to produce characteristic oscilloscopic patterns which serve for the recognition of the half-wave potential.

An oscillographic polarograph based on the Boeke and van Suchtelen circuit has also been described by Prytz and Osterud (*92*).

The Heyrovský-Forejt circuit (*33*) shown in Figure 18 employs a Philips oscillograph Type GM 3156 for a sweep frequency up to 3000 cycles, and Type GM 3152 for a sweep frequency up to 150,000 cycles. A 100-volt, 50-cycle sine wave or square wave alternating voltage is applied across both the cell, M, and a very large variable series resistance, W (1000 ohms to 2 megohms). The resistance, W, is made very large, so that most of the alternating current voltage drop occurs across it rather than the cell, which ensures practically constant current impulses regardless of changes in the back e.m.f. of the cell. A direct current voltage is superimposed on the alternating current voltage across the cell by the potentiometer, E, and this direct current "bias" is adjusted so that the potential of the mercury microelectrode does not vary outside the limits of about 0 and -2 volts versus the saturated calomel electrode during the alternating current cycle. The cell is connected at switch point B to the vertical plates of the oscilloscope, and the frequency of the time sweep is synchronized with that of the applied alternating current voltage, to produce a stationary potential-time figure on the screen.

The resistor, R (1000 ohms), and capacitor, C (0.05 microfarad), provide a means of obtaining the differential of the potential-time curve when the switch is connected to point D. When thus connected, vertical deflection on the oscilloscope screen corresponds to the iR drop across resistance R, and its change with time depends directly on the rate of charging of the capacitor. This is maximal when dE/dt is maximal (midpoint of each branch of the potential-time curve), and minimal at the top of the potential-time curve where dE/dt is zero.

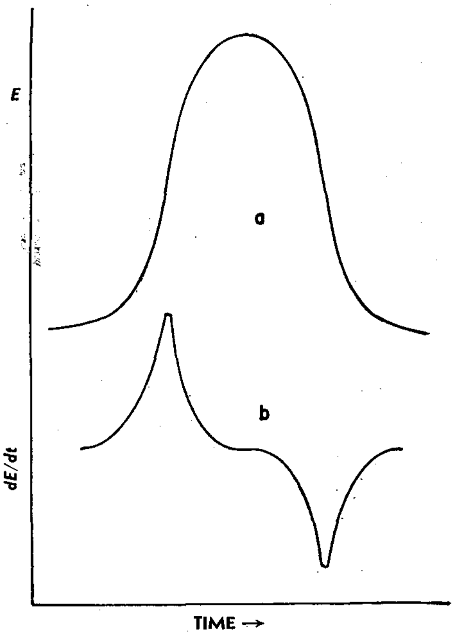

Figure 19. Types of Oscilloscopic Patterns Observed by Heyrovský-Forejt Technique (*33*) in Absence of Reducible Substances

To avoid the complication of the periodically changing area of the dropping electrode, Heyrovský and Forejt performed most of their experiments with the streaming mercury electrode shown in Figure 14.

A typical potential-time trace observed by Heyrovský and Forejt with supporting electrolyte solutions containing no depolarizing substances is illustrated schematically in Figure 19*a*, and Figure 19*b*, is the corresponding differential curve. The left branches of these curves correspond to cathodic polarization and the right branches to anodic polarization (decreasing applied voltage). Since 50-cycle alternating current was used, the time for each complete trace is 0.02 second.

Any process which results in the flow of current at the mercury electrode (change in capacity or electrolytic reactions) produces a horizontal inflection (potential lag) in the potential-time figure. When the electrode reaction occurs very rapidly and reversibly (reduction of lead, cadmium, or thallous ions in dilute nitric acid, and reduction of biplumbite ion in alkaline media), the cathodic and anodic inflections occur at the same potential and the potential-time figure has the symmetrical shape shown in Figure 20*a*. If the reaction does not proceed reversibly, the anodic inflection occurs at a more positive potential than the cathodic one to produce the unsymmetrical type of figure shown by Figure 20*b*. Heyrovský and Forejt observed this unsymmetrical type of oscillogram with zinc in potassium chloride, ammoniacal medium, and strongly alkaline medium, indicating that the reductions of zinc ion, tetrammino zinc ion, and zincate ion are not strictly reversible at the mercury electrode.

When the electrode reaction is very slow no inflections at all are observed. This was the case with the cadmium cyanide complex ion in 1 N potassium cyanide. Although the cadmium cyanide complex produces a normal polarographic wave by the conventional polarographic technique with the dropping electrode, the oscillograms show that its rate of reduction is so slow that no appreciable reduction occurs during the short interval (0.01 second) of each cathodic voltage sweep. It is evident that this oscillographic technique provides a very delicate indication of the relative rates of electrode reactions and it will have many diverse applications.

Because the time lag at the inflection potential (width of the shoulder) increases with increasing concentration of the depolarizer, the Heyrovský-Forejt technique can also serve for quantitative analysis. Heyrovský and Forejt recommend the use of the derivative curve for this purpose. In its present state of development, the technique is neither as sensitive nor as precise as the classical polarographic method, but there is no evident limitation to further refinement.

Numerous examples of the kind of information obtainable with this circuit have been discussed by Heyrovský and his collaborators (*28, 33, 34*).

An oscillographic technique similar to that of Heyrovský and Forejt has been described by Reboul and Bon (*96*).

A review of the principles underlying oscillographic polarography was presented recently by Randles (*94*). The same author and Airey (*3*) described a new type of oscillographic circuit for practical polarographic analysis.

The unique feature of this circuit is that a single voltage sweep is applied to each successive mercury drop during a 1- to 2-second period at a definite time during the drop life. An electronic time-delay circuit actuated by the sudden decrease in current as each drop falls is used to control the instant at which the voltage sweep begins. The remainder of the circuit is similar to that of Matheson and Nichols. The stationary current-voltage figure which appears on the screen of the oscilloscope has the essential characteristics of polarograms obtained by the classical method. The chief difference is the appearance of maxima resulting from the rather long time (1 to 2 seconds) of the voltage sweep. A closer correspondence to classical polarograms, and hence easier interpretation, could probably be achieved by employing a more rapid voltage sweep—e.g., 0.1 second—at a late enough stage during the drop life so that the rate of change of electrode area with time is relatively small. The more rapid voltage sweep produces a larger charging current, but it should be easy to suppress this by electrical compensation. Müller (*85*) has described an oscillographic polarograph utilizing these principles which has been under development at New York University during the past two years.

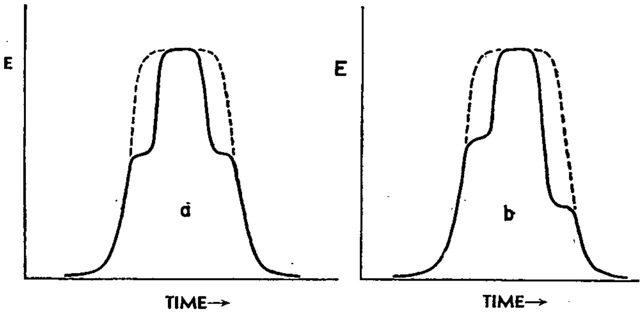

Figure 20. Heyrovský-Forejt Oscillographic Patterns

a, **reversible electrode reactions.** *b*, **irreversible reactions**

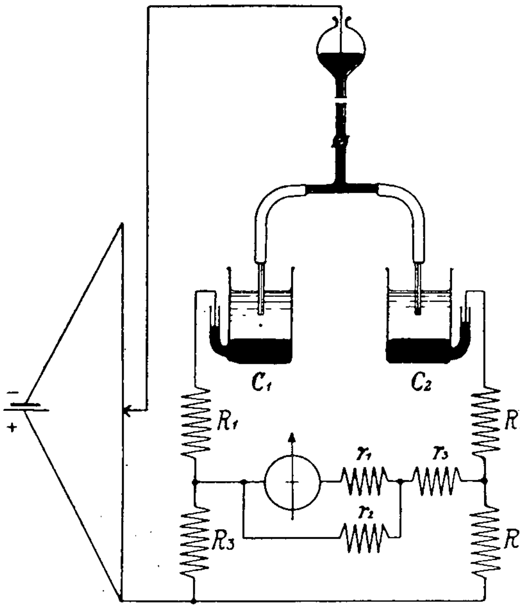

Figure 21. Semerano-Riccoboni Circuit for Differential Polarography (*100*)

Breyer and Gutmann (*12*) and Randles (*95*) have recently reported theoretical and experimental investigations of electrode reactions with superimposed alternating and direct current fields which are of fundamental importance in oscillographic polarography.

DIFFERENTIAL POLAROGRAPHY

Semerano and Riccoboni (*100*) devised the scheme shown in Figure 20 for obtaining differential polarograms.

Two dropping electrodes, as nearly identical in characteristics as possible, are connected in common to the negative side of the polarograph bridge, and each is placed in a separate polarographic cell. The way in which the recording galvanometer is connected into the circuit causes it to register the difference between the potential drops across resistances R_3 and R_4, and hence the difference between the currents that flow through the separate cells. By suitable adjustment of the various resistors, small differences in the characteristics of the two dropping electrodes can be compensated, and the galvanometer made to read zero when the solutions in the two cells are identical. This circuit is an electrochemical analog of the electrical compensation technique.

The circuit was designed primarily for the determination of small amounts of one substance in the presence of much larger amounts of a more easily reducible substance, in which case a polarogram obtained in the ordinary manner would show such a large diffusion current of the major interfering constituent that the wave of the minor constituent would be more or less imperceptible. For this application the unknown solution is placed in one of the cells and the supporting electrolyte alone in the other. The applied e.m.f. is set to such a value that the large diffusion current of the interfering substance is obtained, and a solution of this substance is then added to the "compensating cell" until the galvanometer is restored to zero. When the galvanometer sensitivity is increased, and the polarogram recorded, only the wave of the minor constituent appears. It is unnecessary to remove dissolved air, as the oxygen currents will be compensated.

If it were possible to synchronize the drop formations exactly at the two electrodes this would be an elegant, generally useful technique. Actually, however, such synchronization is virtually impossible. Consequently the "compensated zero" undergoes rhythmic positive and negative shifts due to the periodic change in phase of the mercury drops, and this is reflected by a corresponding succession of nodes in the recorded polarogram. This beaded string effect can be minimized by using electrodes of very short drop time, but the Ilkovič equation then fails seriously.

The circuit shown in Figure 21 was devised by Heyrovský (*29*) for obtaining the derivative $\Delta i/\Delta E$ of the ordinary current-voltage curve.

It comprises two dropping electrodes (or better, streaming mercury electrodes) dipping in the same polarographic cell but connected across an end resistance in the polarograph bridge so that their potentials differ by a constant amount, ΔE, as the total applied e.m.f. is increased. According to Heyrovský, the galvanometer placed in parallel with the two electrodes and their series resistors indicates the difference in current flowing in the two electrode circuits. The resulting recorded curve is a plot of $\Delta i/\Delta E$ versus E. Maxima appear at the half-wave potential of each substance in the solution, and the diffusion current plateaus are represented by minima. The heights of the maxima in the derivative curve are proportional to the concentrations of the respective substances. When used with dropping electrodes, the periodic phase shift of the dropping rates produces the same nodes observed with the Semerano-Riccoboni circuit, and to eliminate this nuisance Heyrovský recommends the use of streaming mercury electrodes.

Heyrovský pointed out that substances whose reduction potentials are so close to the final current rise that a distinct wave does not appear on an ordinary polarogram can be detected unequivocally by the differential technique—e.g., sodium ion in the presence of a large excess of lithium ion. The circuit may also be useful for determining small amounts of a more difficultly reducible substance in the presence of more easily reducible major constituents, but quantitative data have not yet been obtained.

Kanevskiĭ (*40*) has also described a differential polarographic technique which permits compensation of both electrolytic and non-Faradaic currents.

STANDARDIZED DIFFUSION CURRENT CONSTANTS

It has long been the custom in practical polarographic analysis to calibrate empirically the particular dropping electrode used with known concentrations of the substance being determined, and this procedure is capable of yielding results of higher precision and accuracy than any other technique. However, it is time-consuming and entails the inconvenience of stocking standard solutions of each substance to be determined.

Lingane (*58*) has shown that empirical calibration can be dispensed with, and polarographic analysis placed on a more "absolute" basis, by employing standardized diffusion current constants, I, experimentally defined by $i_d/(Cm^{2/3}t^{1/6})$ and theoretically equal to 605 $nD^{1/2}$ at 25° C. The diffusion current constant is characteristic of the particular reducible substance in a given supporting electrolyte at a given temperature and is virtually independent of the characteristics of the dropping electrode, provided the drop time is greater than about 2 seconds. Hence, if the diffusion current constant, I, for the substance being determined is known, its concentration may be computed from the measured values of i_d, m, and t by the relation

$$C = \frac{i_d}{Im^{2/3}t^{1/6}} \tag{14}$$

The principle of this method is somewhat similar to the "step quotient" method of Forsche (*22*), but it is capable of more general application.

Because it is much simpler to measure m and t for a given dropping electrode than to calibrate with known concentrations at each time of use, the use of standardized diffusion current constants is particularly well suited to rapid routine analyses. Lingane has listed experimental values of the diffusion current constants of a number of metal ions in various commonly used supporting electrolytes. Because the diffusion current "constant" actually changes slightly with capillary characteristics, this technique is subject to a small error. Fortunately, the variation of I with capillary characteristics is small enough when the drop time is in the usual range of 2 to 6 seconds that the uncertainty caused by it usually does not exceed ±2%, and this degree of accuracy is ample for most practical purposes. Furthermore, it is a simple matter to employ a dropping electrode whose characteristics are so close to those of the electrode that was used originally to evaluate the diffusion current constant that the error caused by different capillary characteristics becomes vanishingly small.

When the temperature coefficient of I is known, the use of a constant temperature bath is unnecessary, and one may simply measure the temperature of the solution and apply the corresponding value of I in computing the concentration. As (dI/dT) is generally about 2% per degree, the temperature should be read to ±0.1° C.

Taylor (*107*) has recently reviewed the relative merits of the foregoing absolute method and several well known comparative techniques of quantitative polarographic analysis. In particular he calls attention to the advantages for calibration purposes of using standard analyzed samples whose composition closely approximates the samples to be analyzed. This practice has much to recommend it, and for routine analysis of technical materials the carefully analyzed samples distributed by the National Bureau of Standards can be used as standards in many cases.

ELECTROLYTIC SEPARATIONS PRIOR TO POLAROGRAPHIC ANALYSIS

The nature of the polarographic method makes it especially valuable for the determination of small or trace amounts of one or more metals in the presence of large amounts of others. By judicious choice of supporting electrolytes, and utilization of complex formation to "mask" major interfering constituents, it is sometimes possible to avoid preliminary separations. However, this procedure is limited, and in most analyses of complex materials some preliminary separations are usually required.

The removal of interfering metals by electrolysis has a number of practical advantages over the more usual methods based on precipitation. Electrolytic separations do not require the introduction of large amounts of reagents which may complicate subsequent polarographic determinations, the ever-present danger of loss of minor constituents by coprecipitation is avoided, and, when the cathode potential is properly controlled, they are highly selective. The recent development of potentiostats (*15, 35, 61*) which maintain the potential of a working electrode constant has made the performance of controlled potential separations so nearly automatic that less operator time is required than in precipitation methods.

It has been demonstrated (*57*) that a mercury cathode is more advantageous than a platinum cathode for controlled potential electrolytic separations, because the optimum potentials and other conditions are easily and reliably deducible from the known polarographic characteristics of the metals in question. Furthermore, it is possible to achieve sharper separations with a mercury cathode.

Lingane (*59*) developed a systematic procedure for the analysis of mixtures of copper, bismuth, lead, and cadmium, in any proportion, based on controlled potential separations with the mercury cathode from an acidic tartrate solution. The several metals may be successively separated, and a small sample of the solution after each separation is transferred to a polarographic cell for analysis.

Controlled potential separations with a platinum cathode have been employed in connection with the polarographic determination of lead, tin, nickel, and zinc in copper-base alloys (*62*). Two samples are used; from one of these copper is removed prior to the determination of lead and tin, and from the other copper, lead, and tin are removed prior to the determination of nickel and zinc. The separations are made from 0.5 *M* hydrochloric acid, a complete analysis requires only about 2 hours, and accurate results are obtained.

Electrolysis with a mercury cathode is especially useful and convenient for separating large amounts of more easily reducible metals from elements like aluminum, uranium, vanadium, and the alkali metals, which are not reduced to the elemental state at a mercury cathode in dilute acid medium. In such cases it is not necessary to control the potential. Lingane and Meites (*68*) developed a method using this principle for the rapid and accurate determination of vanadium in steels and ferroalloys. Electrolytic separations with a mercury cathode have also been recommended by Johnson, Weaver, and Lykken (*38*), who developed a convenient immersion type of mercury cathode, and by Rabbitts (*93*), who described an improved form of the Melaven type cell. The optimum conditions for the removal of such metals as iron, copper, zinc, nickel, cobalt, chromium, lead, tin, and molybdenum by constant current electrolysis with a mercury cathode have been studied by Parks, Johnson, and Lykken (*90*).

The Precision Scientific Co. has recently placed the Johnson-Weaver-Lykken apparatus on the market under the name Mercalyzer. This instrument serves only for constant current electrolytic separations with the mercury cathode, and its usefulness is limited because no provision is made for separations by the more versatile controlled cathode potential technique.

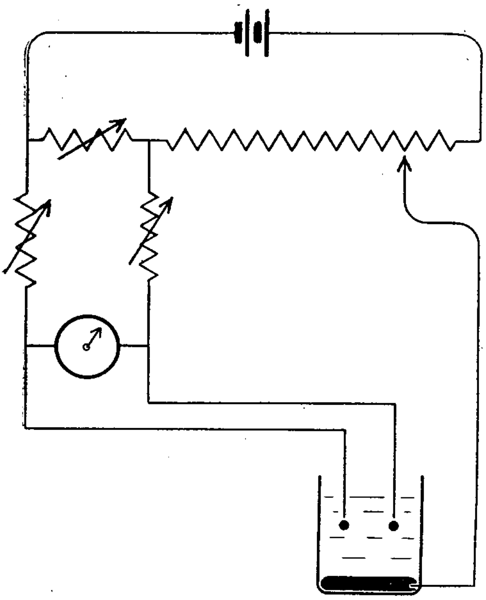

Figure 22. Heyrovský Circuit for Differential Polarography (*29*)

Electrolysis is usually employed to remove interfering metals, leaving in solution the small amounts of metals to be determined, but the converse technique of concentrating the metals to be determined by preliminary electrodeposition is advantageous in determining small or trace quantities. This principle was recently applied by Furman, Bricker, and McDuffie (*24*) in connection with the determination of trace quantities of a number of different metals present as impurities in various substances. The metals were deposited in a small mercury cathode, the mercury was removed by distillation, and the residue was taken into solution and examined polarographically.

COULOMETRIC ANALYSIS

The classical methods used to identify the reduction of oxidation states corresponding to polarographic waves include the comparison of observed diffusion current constants with the values predicted from the Ilkovič equation for various assumed values of n, comparison of wave heights with substances of known n-value, and calculation of n from the slopes of polarographic waves. The first two methods, which are essentially the same in principle, require a knowledge of the diffusion coefficient of the substance in question, which is usually only known approximately, and they fail in complex reductions where the n-value is large. The last method can be employed only when the reduction or oxidation is known to occur reversibly at the dropping electrode, and since the wave slope is very sensitive to a variety of other factors, this method is very limited and its reliability must always be questioned.

The most generally applicable and reliable procedure for determining n in complex reductions and oxidations is based on the newly developed technique of coulometric analysis (*65*).

A solution of known concentration of the substance is electrolyzed with a large mercury cathode whose potential is controlled at a value corresponding to the diffusion current plateau of the wave in question. Under these conditions the reduction occurs with 100% current efficiency and the current ultimately decreases to virtually zero. The quantity of electricity passed, Q, is measured by a coulometer in series with the cell, and since the number of moles, N, of the substance is known, n is given by Q/N. Although the n-values will be the same, the actual product of the large scale reduction may be different from the product produced at the dropping electrode, because of the longer time available for secondary reactions subsequent to the actual reduction.

The technique has been applied to organic substances, such as picric acid (*65*) and iodophenylacridine (*71*), and has proved valuable for elucidating the complex polarographic chemistry of molybdenum (*18*), tungsten (*103*), selenium, and tellurium (*69*).

ZERO CURRENT POTENTIAL OF DROPPING ELECTRODE

An isolated dropping mercury electrode in a supporting electrolyte that is entirely free of reducible or oxidizable substances acquires a potential corresponding to the maximum on the electrocapillary curve of mercury (−0.6 volt versus the saturated calomel electrode in chloride solutions). If the potential is forced by an applied e.m.f. to assume some other value, a continuous current is observed to flow due to the establishment of the electrical double layer on the continuously forming surface. This is the familiar "charging current" or "condenser current" which is zero at the potential of the electrocapillary maximum, which becomes increasing anodic when the potential is made more positive than the electrocapillary zero, and increasingly cathodic when the potential is shifted in the negative direction. The slope, di/dE, of the charging current curve is so small that an exceedingly slight cathodic current resulting from a mere trace of a substance which is reduced at a potential more positive than the electrocapillary zero produces a relatively large positive shift in the potential at which the observed current is zero. Conversely, a trace of a substance which is oxidizable at a potential more negative than the electrocapillary maximum will produce a large shift of the zero current potential in the negative direction.

Laitinen, Higuchi, and Czuha (*53*) have recently utilized this principle to develop a sensitive method for the determination of traces of oxygen in gases or in solution.

These authors showed that the shift, $E - E_{\text{max.}}$, of the zero current potential increases with time during the life of the mercury drop according to

$$E - E_{\text{max.}} = 17.2\ C\ t^{1/2} \qquad (15)$$

where C is the concentration of oxygen in millimoles per liter, t is expressed in seconds, and the constant includes the capacity of the double layer, the diffusion coefficient of oxygen, and certain geometrical constants. A high capacity condenser was inserted in the measuring circuit, so that the observed value of $E - E_{\text{max.}}$ corresponded to the maximal value during the drop life. A special flow-type cell was designed to provide rapid equilibration of the supporting electrolyte (0.1 or 1 M potassium chloride) with the gas being tested. When a small amount of a maximum suppressor, such as methyl red, was present the observed shifts of the zero current potential were linear functions of oxygen concentration up to about 1% by volume in the gas mixture, and amounts of oxygen as small as 0.01% could be detected.

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ORGANIC POLAROGRAPHY

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THE past 8 years have seen considerable advancement in the field of organic polarography. Developments were of three types: reinterpretation of previous work; investigation of the oxidation and reduction of new types of organic compounds; and applications of the polarographic method to quantitative estimation, structure determination, and preparation of organic compounds.

The polarographic investigations in most cases have been carried out more carefully and more completely than in the past and the half-wave potential has been accepted as a standard measurement. The interpretation of the nature of the reduction and of the reduction products in irreversible systems leaves much to be desired. There is a tendency to base the interpretations solely on the number of electrons involved in the reduction with no regard for organic chemistry. Often well known compounds which might react further, are postulated as end products without being studied polarographically.

The majority of the work has been carried out in mixtures of water and organic solvents. In nonaqueous media such as acetic acid (*5*), formamide, ethyl alcohol, methyl alcohol, glycerol (*102*), and ethylene glycol (*46*), the waves are lower and in some cases more drawn out than those obtained for the same concentration in water.

As supporting electrolytes the tetralkylammonium salts have proved useful (*101*), since they have made possible the investigation of compounds reducing at potentials more negative than that of the alkali metals.

REVERSIBLE SYSTEMS

The study of reversible systems has been extended and in general found to give results at the dropping mercury electrode which are similar to those obtained potentiometrically. In certain cases, however, such as methylene blue (*24*), riboflavin (*25, 26*), 1-hydroxyphenazine (*81*), and pyocyanine (*30, 128*) the behavior is slightly different in that a small anomalous reduction wave is found to precede the main wave. The latter's half-wave potential is in agreement with the potentiometrically determined potential while that of the anomalous wave occurs at a more positive potential. Evidence presented (*23*) indicates that this phenomenon is due to the adsorption of the reduced form on the drop with the energy set free by the adsorption process aiding the reduction in the same manner as the electrodeposition of metals on mercury is facilitated by the energy of amalgam formation. If the oxidized form of the redox system is adsorbed as with phenosafrine, a small wave appears at more negative potentials than the main wave. When both forms are adsorbed equally, no effect is noticed on the polarographic waves.

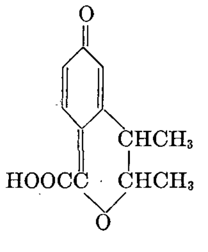
The adsorption waves are independent of the concentration above a certain limit, directly proportional to the height of the mercury reservoir, are decreased with increase in temperature (*23*), and are suppressed by eosine and other compounds which are more strongly adsorbed but which are not reduced polarographically. These suppressors in addition shift the reduction waves of reversible systems to more negative potentials and decrease the heights of the waves (*144*) and may, if they are large in molecular weight like horse albumin, reduce the diffusion current to exceedingly small values (*57*).

The adsorption phenomena do not occur with benzoquinone or duroquinone (*82*) but have been observed with irreversible systems such as colchicine (*23*) and a styrene-oxygen polymer (*20*). In the latter case desorption occurs and produces a decrease in the diffusion current past −1.5 volts.

Polarographic studies have been made of vitamin K (*53*), alkyl substituted napthoquinones (*105*), α-tocopheryl quinone (*115*), anthraquinones (*34, 45*), and toluquinones related to mold metabolites (*85*). In the last example no definite relationship was found between the half-wave potentials and the antibacterial activity.

The polarographic method has been used to follow the effect of ultraviolet light on quinones (*91*).

Methylene quinone systems which occur in citrinin (I) (*55, 85*), fuchsones (II) (*119*), and the colored forms of phenolphthalein (III) (*68*) and fluorescein (*36*), are irreversible even though they resemble quinones in structure. Thus, introduction of substituents into fuchsone produces no shift in half-wave potential. This behavior parallels that observed with benzophenone rather than with benzoquinone (*119*).



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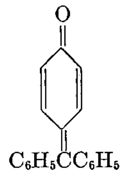

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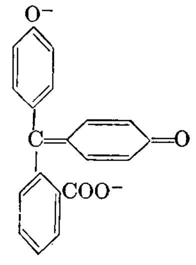
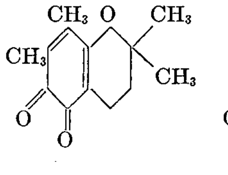


III

The half-wave potential obtained with the red form of phenolpthalein does not shift with pH (*68*).

o-Quinones that have been studied are 2,2,7,8-tetramethylchroman-5,6-quinone (IV) (*115*), adrenchorome (V) (*141*) obtained by the enzymatic oxidation of adrenalin, and the *o*-quinone (VI) (*142*) obtained by a similar process on tyrosine. The results obtained from the last two indicate that the *o*-quinone system is reversible at the dropping mercury electrode. This system is difficult to study because of the instability of these compounds and the side reactions that take place. Adrenalin (*106*) and catechol (*126*), the hydroquinones in this series, give anodic waves with half-wave potentials that shift 0.059 volt per pH unit.



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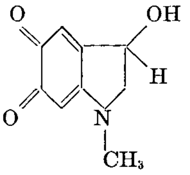

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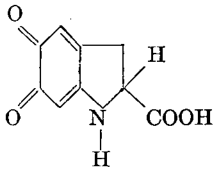


VI

Results obtained with azobenzene indicate that it is irreversibly reduced at the dropping mercury electrode since the half-wave potential is independent of pH (*127*). These results should be confirmed by a study of the reduction product, hydrazobenzene, since the azo system is complicated by cis-trans isomerism (*138, 145*) and the formation of salts in acid solution. A small but definite difference in the ease of reduction of the cis and trans isomers is obtained and has been used to show, in agreement with x-ray studies, that the green α- and red β-*p*-azophenols are not cis-trans isomers (*72*).

IRREVERSIBLE SYSTEMS

Aldehydes. Formaldehyde shows a different behavior from the other aliphatic aldehydes because the following equilibrium is mainly over to the right.

$$H_2C{=}O + H_2O \rightleftharpoons H_2C(OH)_2$$

Since only free formaldehyde is reducible, the diffusion current is limited by the speed of the dehydration (*11*, *125*) and subsequently by factors which influence the equilibrium such as temperature, pH, solvents (*15*), and buffers (*125*). This mechanism is consistent with oscillographic measurements of the polarographic potential time curves (*12*) and with the observation that the diffusion current is independent of the height of the mercury column above the cathode (*13*). Proportionality between the diffusion current and concentration is obtained only if the solution is well buffered and if enough maximum suppressor such as lanthanum ions are present (*14*).

Acetaldehyde (*16*) and propionaldehyde (*17*) give waves which are less dependent on external factors since the aldehydes are hydrated less than formaldehyde.

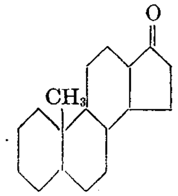
The polarographic method has been used to determine formaldehyde in the presence of other aldehydes (*140*) and the amount of acetaldehyde produced in the conversion of ethanol to butadiene (*38*); it can be used indirectly to determine compounds which are converted into acetaldehyde and formaldehyde by periodic acid. This variation has been used to determine *d*-serine in protein hydrolyzates (*21*), ethylene glycol, and 1,2-propylene glycol (*129*).

Among the hydroxyaldehydes, glycollic aldehyde (*17*) and the aldoses (*143*) give waves which are similar to that of formaldehyde in that they are strongly dependent on pH and temperature. Glycollic aldehyde is present in equilibrium with its hydrate whereas the aldoses (also ketoses) are present mainly as cyclic hemiacetals. In both cases therefore the polarographic wave is dependent on the velocity of the formation of the free aldehyde form at the electrode.

Unsaturated aldehydes in which the aldehyde group is conjugated with one or more double bonds, give two reduction waves in all cases. The first wave for acrolein (*80*) and crotonaldehyde represents a bimolecular 1,4-reduction and is followed by the reduction of the aldehyde group. With higher aliphatic polyene aldehydes, such as 2,4-hexadienal, 2,4,6-octatrienal, 2,4,6,8-decatetraenal, and 2,4,6,8,10-dodecapentaenal, in view of the fact that a second wave is obtained, it seems more probable that either a 1,4- or a 1,*X*- addition is involved and not a 1,2- addition as has been proposed (*41*).

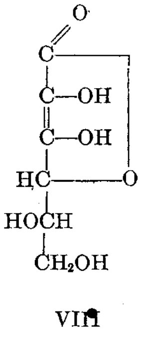
Acrolein can be determined in the presence of saturated aldehydes (*47*, *80*). Both waves are suitable if formaldehyde is present but only the first wave can be used with acetaldehyde (*80*).

The mechanism of reduction of benzaldehyde has been confirmed by controlled electrolytic reduction. The first wave represents the formation of hydrobenzoin while the second is due to the formation of benzyl alcohol (*88*).



VII

Ketones. Aliphatic or cyclic ketones are not reduced directly in ammonium chloride solution but give waves if present as hydrazones, phenylhydrazones (*77*), or Girard derivatives (*146*). The reduction of the Girard derivatives is specific for cyclopentanone and substituted cyclopentanones and does not work with cyclohexanones. This method is suitable for the determination of 17-ketosteroid (VII) (*146*) in both urinary and tissue extracts (*18*). It shows smaller variations due to technique than the colorimetric method (*8*). Interfering substances can be removed by oxidation with potassium permanganate (*7*). This method can also be used for 17-hydroxysteroids if these are oxidized beforehand by aluminum *tert*-butoxide (*53*). Maleic acid monohydrazide and aminoguanidine can be substituted for Girard's reagent but offer no advantage over this compound (*9*).



VIII

Acetophenone (*133*), methoxyacetophenones (*6*), and diacetoresorcinols (*109*) give two reduction waves at the dropping mercury electrode. The ratio of the heights of the two waves of acetophenone are changed if the determination is carried out in the presence of benzalacetone but the sum remains the same as when investigated alone (*133*).

Benzophenone, which gives two waves (*1*), upon controlled electrolytic reduction forms benzpinacol and benzhydrol, respectively (*88*).

Both aliphatic and aromatic ketones conjugated with a double bond or another ketone group are reduced at the dropping mercury electrode. Benzalacetophenone (*89*) and both isomeric dibenzoylethylenes (*59*) have been studied. The trans form of the latter is more easily reduced than the cis isomer. Dibenzoylmethane (*89*) and β-ketoaldehydes (*110*) behave like α,β-unsaturated carbonyl compounds and must be reduced through the enol form.

This method has been used to follow the formation of methyl vinyl ketone from methylvinylcarbinol (*43*) and to determine santonin (*103*) and steroids which are α,β-unsaturated ketones (*104*) or which can be rearranged or oxidized to this structure by aluminum *tert*-butoxide (*54*).

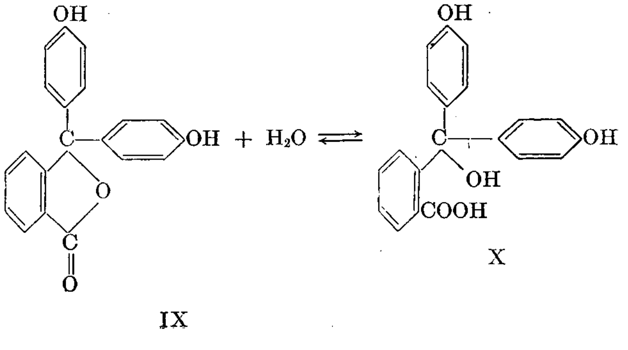
α-Diketones such as biacetyl and benzil are reduced to acetoin and benzoin, respectively. In alkaline borate buffer the concentration of benzil is decreased by complex formation (*87*).

The reduction of biacetyl has been used to follow the vapor phase oxidation of 2,3-butylene glycol (*43*) and to determine acetoin in blood and urine (*49*). The acetoin is oxidized to biacetyl first with ferric chloride.

Acids. Organic acids with a reducible group are more easily reduced than the corresponding anion. Such acids give one or two waves depending upon the pH of the solution and the dissociation constant of the acid. As in other rate processes the diffusion current is independent of the height of the mercury reservoir (*27*). This phenomenon has been observed in the reduction of phthalic acid (*44*) and is the actual explanation for the two waves observed with pyruvic acid. These waves which were once attributed to keto-enol tautomerism, are obtained also with benzoylformic acid which cannot enolize (*22*). Mesoxalic acid behaves differently and gives no reduction wave due to hydration. The hydrazone and oxime, however, are reduced and give waves involving two electrons (*108*).

Esters containing a reducible functional group behave normally and give only one wave (*22*). If the esters are derived from β-dialkylaminoethanol as in local anesthetics, a catalytic hydrogen wave is obtained (*78*).

Hydroxy acids give only hydrogen waves. The lactones from these compounds, however, in both the aliphatic and aromatic series undergo reduction. If an ene-diol structure is present as in vitamin C (VIII), an anodic wave can be obtained (*31*). A reduction of the lactone form (IX) must occur with phenolphthalein at



IX

X

a pH less than 8 rather than of the hydrolysis product (X), as is postulated (*68*), since compounds like triphenylcarbinol which are related to (X), are not reduced at the dropping mercury electrode.

These results have been used to follow the formation of lactones from polyhydroxyacids (*79*), to determine vitamin C in fruits and vegetables (*48*) and to determine the structures of esters and amides of γ-ketoacids such as *o*-benzoylbenzoic acid (*135, 136*) and 3-(*p*-bromobenzoyl)-3-methylacrylic acid (*137*).

Acids conjugated with a double bond are reducible. The reduction is sensitive to structural modifications so that maleic acid can be determined in the presence of fumaric acid (*130*) and fumaric acid in the presence of aconitic and citraconic acids (*93*).

This method has been used to determine the purity of α,β-unsaturated acids (*35*), to follow the depolymerization of aconitic acid (*93*) and the reduction of maleic acid to succinic (*112*), and to determine the amount of unchanged maleic anhydride in styrene-maleic anhydride and vinyl acetate-maleic anhydride polymerizations (*139*).

Organic Halides. Halogen atoms on a carbon atom alpha to a carbonyl group or phenyl group, positive halogens, halogen attached to a metal, and aromatic iodides are reducible at the dropping mercury electrode. Examples that have been studied are ω-bromoacetophenone, benzyl bromide (*89*), chloramine T (*52*), 9-(*o*-iodophenyl)acridine (*76*), iodofuchsone (*119*), 3,5-diiodotyrosine and thyroxine (*113*), and triethyllead chloride (*97*).

Results reported for 1,1,1-trichloro-2,2-diphenylethane, triphenylmethyl chloride, and related compounds are so varied (*58*) that side reactions must occur under the conditions used, and cause the deviations observed. The waves observed for 1,1,1-trichloro-2,2-diphenylethane, substituted 1,1,1-trichloro-2,2-diphenylethanes, and triphenylmethyl chloride are due to hydrogen chloride formed by decomposition of the 1,1,1-trichloro-2,2-diphenylethanes or by hydrolysis of triphenylmethyl chloride in 80% ethanol. The close similarity in half-wave potentials of 1,1-di-*p*-chlorophenyl-2,2-dichloroethene and 1,1-di-*p*-chlorophenyl-1,2,2,2-tetrachloroethane suggests that the mercury present may remove two chlorine atoms from the latter and form the former. The reduction observed is of the double bond and not of the halogens as reported. The behavior of hexachlorocyclohexane (−1.8 volts, saturated calomel electrode) suggests the reduction of an allylic halide formed by the loss of chlorine or hydrogen chloride since the ease of reduction approximates that of allyl chloride (−2.00 volts, saturated calomel electrode).

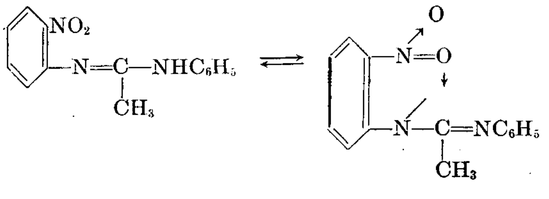
Nitro Compounds. Nitro groups are reducible in both the aliphatic and aromatic series. The reduction in the aliphatic series proceeds in one step at approximately the same point in either 0.05 *M* sulfuric acid or 0.05 *M* sodium sulfate (*37*). In buffers with a pH of 4.5 or greater two waves occur. The first wave represents the reduction to the hydroxylamine since the second wave is only half as high and is similar to that observed with *N*-methylhydroxylamine and hydroxylamine. The second wave disappears in more alkaline solutions. No reduction is observed for the aci form (*90*).

The interpretation of the reduction of aromatic nitro compounds in certain cases is questionable since phenylhydroxylamines have been proposed as final reduction products without studying their stability in the buffers used or their behavior at the dropping mercury electrode. Thus, phenylhydroxylamine in alkali rearranges to azoxybenzene and aniline (*73*) and is oxidized very easily by air to azoxybenzene. $3C_6H_5NHOH \longrightarrow C_6H_5\underset{\underset{O}{\downarrow}}{N}{=}NC_6H_5 + C_6H_5NH_2 + 2H_2O$. The former is reduced at the dropping mercury electrode and gives a wave involving four electrons. Such a phenomenon probably occurs with *p*-hydroxylaminobenzenesulfonamide which is reducible only in 0.1 *N* sodium hydroxide (*74*). The half wave potential observed is similar to that observed with *p,p'*-azoxybenzenesulfonamide.

Phenylhydroxylamines also rearrange in acid solution and give *p*-aminophenols. This may be the reason why only a four electron reduction is observed for each nitro group of *m*-dinitrobenzene in acid media (*67*).

Stable phenylhydroxylamines are reported to be formed from *o*-nitrophenol (*3*) and *o*-nitrocresols (*2*) in solutions of pH less than 6. In buffers between pH 6 and 9.5, mixtures with the amine are formed whereas in buffers more alkaline than 9.5 only the amine is produced. Since the corresponding para compounds are reduced to the amines in all the buffers, it has been suggested without experimental confirmation that the intermediate hydroxylamines from the *o*-nitrophenols are stabilized towards further reduction to the amines by hydrogen bonding. The normal reduction of nitrodihydroxybenzenes (*4*) to the corresponding amines, regardless of the position of the nitro group, suggests that some other explanation must account for the abnormal behavior of *o*-nitrophenol and the *o*-nitrocresols.

More conclusive evidence for hydrogen bonding is the more positive half-wave potential observed with the *o*-nitrophenols than with the corresponding para compounds (*3*). A similar effect has been found with *N*-phenyl-*N'*-nitrophenyl acetamidines (XI) and suggests a stabilization of one tautomer (XII) in the *o*-nitro compound (*100*).



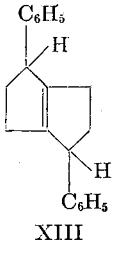
XI XII

The polarographic method has been used successfully for the determination of from 0.01 to 0.05% of nitrobenzene in aniline with an accuracy of better than 4% (*50*).

Nitroso Compounds. The nitroso group behaves normally and is reduced to an amino group in *p*-nitrosophenol (*3*) and *N*-nitrosophenylhydroxylamine. In the latter case phenylhydrazine is formed in acid solution while *N*-aminophenylhydroxylamine is formed in alkaline solution (*69*).

Unsaturated Hydrocarbons. Phenyl substituted olefins and acetylenes (*71*) and aromatic polynuclear hydrocarbons (*134*) are reducible at the dropping mercury electrode. Half-wave potentials are obtained which are independent of pH, very sensitive to structural variations, and parallel the ease of addition of sodium to these compounds. Thus it is possible to distinguish between cis and trans isomers. *Cis*- or isostilbene is reduced at more negative potentials (−2.18 volts) than the trans compound (−2.13 volts) in 80% alcohol (*138*).

This method has been used to prove the location of the double bond in the 2,6-diphenylbicyclo-(3,0,3)-octene (XIII) system (*131*), to determine the amount of naphthalenes in petroleum fractions boiling in the kerosene or light gas oil range (*29*), and to establish the mechanism of the addition of sodium to 1,1-diphenylethylene and related compounds (*132*). In connection with this problem triphenylmethyl was investigated and found to be reducible at the dropping mercury electrode.

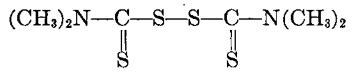


XIII

α,β-Dimethylstilbene, diethylstilbestrol, and dienostrol are reported not to reduce in 70% dioxane containing tetraethylammonium bromide up to −2.9 volts (*138*). These compounds should be reinvestigated since α,β-diethylstilbene gives a normal wave (−2.55 volts, saturated calomel electrode) in 75% dioxane containing 0.175 *M* tetrabutylammonium iodide.

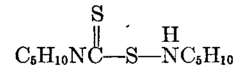
Peroxides. Peroxides show a normal behavior at the dropping mercury electrode unless present in high concentrations in hydrochloric acid solutions. Under these conditions decomposition occurs and forms mercurous chloride which is reported to cover the anode and to interfere with the determination (*84*). Peroxides that have been studied are methyl and ethyl hydroperoxide, diethylperoxide, cyclohexene peroxide, acetone triperoxide (*84*), *tert*-butyl peroxide (*20*), and ether peroxide (*96*). The results obtained have been used to show that the autoxidation of ether produces no hydrogen peroxide (*95*) and that the styrene-oxygen polymer has a peroxide structure (*20*).

Sulfur Compounds. The disulfide linkage is apparently the only sulfur grouping that can be reduced at the dropping mercury electrode. The reduction occurs not only when the disulfide group is attached to alkyl groups, but also when joined to thiocarbonyl groups as in tetramethylthiuramdisulfide (XIV). The reduction in the latter case may be of the dithiocarbamic acid grouping since the piperidine salt of pentamethylene dithiocarbamic acid (XV) gives a reduction wave (*92*).



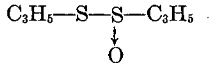
$(CH_3)_2N{-}\underset{S}{\underset{\|}{C}}{-}S{-}S{-}\underset{S}{\underset{\|}{C}}{-}N(CH_3)_2$

XIV



$C_5H_{10}N\overset{S}{\overset{\|}{C}}{-}S{-}\overset{H}{N}C_5H_{10}$

XV



$C_3H_5{-}S{-}\underset{O}{\underset{\downarrow}{S}}{-}C_3H_5$

XVI

The reduction of allicin (XVI) (*32*) must be of the disulfide link since sulfoxides (*117*) are not reducible.

The thiol group gives anodic waves and also will produce catalytic hydrogen waves in ammoniacal cobalt solutions at −1.8 volts if present on the alpha carbon atom of an acid or on the beta carbon atom of an amino acid (*42*). No wave is observed with mercapto alcohols such as BAL. Apparently this catalytic effect is not solely characteristic of the thiol grouping since certain amino acids show the same effect but to a smaller degree (*99*).

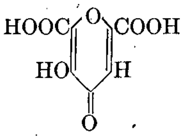
The catalytic wave has been used to determine proteins and cystine in urine (*94*) and is the basis for determining a protein index which is useful for routine analysis of blood proteins (*83*).

Heterocyclic Compounds. The simple five-membered heterocyclic ring systems furan (*70*) and pyrrol (*111*) are not reducible at the dropping mercury electrode. The interpretation of the reduction of aucubin hexaacetate, a naturally occurring furan of unknown structure, in this manner (*56*) is questionable. Aldehyde groups attached to these rings or the reduced ring as in streptomycin (*75*) behave normally. Ketones have been investigated only in the pyrrol series and are reducible only if the group is present in the α-position (*19*).

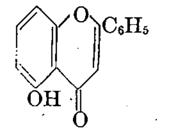
No studies are reported on indole but alkaloids like brucine, strychnine, egometrine, ergotoxine, physostigmine, and yohimbine, which contain this ring system give catalytic hydrogen waves (*63*).

N-acetylcarbazole behaves like *N*-acetylpyrrol and is not reduced (*86*).

Six-membered ring systems containing one hetero atom have been studied more intensely. Pyrones as exemplified by meconic acid (*61*) (XVII) from opium, and flavones (*39*) are reducible. The reduction in both cases involves the carbonyl group and not the double bond conjugated with it since a hydroxyl group in the 5-position (XVIII) decreases the ease of reduction.

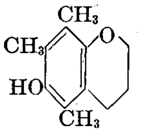


XVII

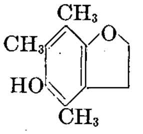


XVIII

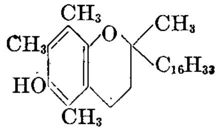
6-Hydroxy-5,7,8-trimethylchromans (XIX) give anodic waves which differ by 10 millivolts from 5-hydroxy-4,6,7-trimethylcoumarans (XX) and have been offered as proof for the chroman structure of vitamin E or α-tocopherol (XXI). This method also can be used successfully for the quantitative estimation of α-tocopherol (*114*) but fails in the presence of 2% fat (*10*).



XIX

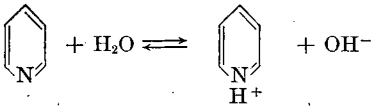


XX

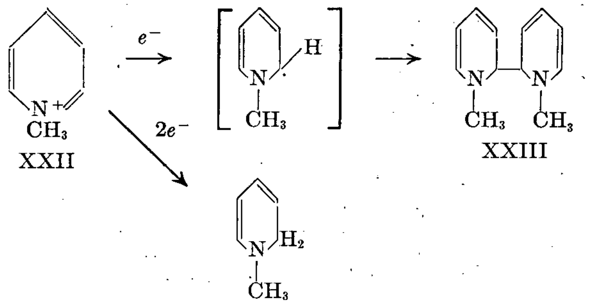


XXI

Pyridine gives a catalytic hydrogen wave which is actually due to the pyridinium ion formed. Since this ion is in equilibrium with the free base, the height of the wave is dependent upon pH (*66*, *120*) and the strength of the pyridine concerned as a base. Thus as the buffer becomes more alkaline, the catalytic wave becomes smaller and eventually disappears. Unsaturated groups if present give reduction waves which are usually observed only in alkaline buffers but may in some cases precede the catalytic wave.



Replacement of the hydrogen on the nitrogen by a methyl group, as in methylpyridinium hydroxide (XXII), gives a true reduction wave which is independent of pH and has a slope of 0.063. This wave may be followed by a second wave which shifts with pH and is due either to the reduction product (XXIII) which can now behave like pyridine and give a catalytic hydrogen wave, or may be a reduction of the methylpyridinium ion (XXII) to *N*-methyldihydropyridine (XXIV) (*121*).



XXII XXIII

XXIV

The same type of behavior is observed with other pyridine derivatives such as nicotinic, picolinic, and isonicotinic acids (*122*), their methchlorides (*123*), nicotinamide and its methchloride (*124*), piperidine, quinoline (*66*), quinine, cinchonine, cinchonidine, quinidine (*63*), quinaldinic acid (*116*), papaverine, narcotine, cotarnine, morphine, codeine, ethylmorphine, apomorphine (*63*), hydrastine, hydrastinine, berberine, emetine, cephaeline (*62*), hyoscine, atropine, hyoscyanine, homatropine, cocaine, nicotine, and sparteine (*64*).

The catalytic hydrogen waves are useful for the quantitative estimation of codeine, cocaine, hyoscine (*60*), morphine, diamorphine, emetine, strychnine, and atropine (*65*), but are of no value for the identification of these compounds.

Acridines because of their feeble basic properties behave differently from pyridine and are reduced to 9,10-dihydroacridines. This mechanism has been confirmed by a controlled electrolytic reduction of 9-(*o*-iodophenyl)acridine. This process can be carried out selectively without removing the iodine atom (*76*).

The half-wave potentials of various aminoacridines have been found to be related to their chemotherapeutic activity. Compounds having a more negative reduction potential than −0.400 volt (normal calomel electrode) proved to be the most active antiseptics (*28*).

Other heterocyclic compounds such as vitamin B_1 (*107*), adenine, adenosine, adenylic acid (*51*), xanthopterin, rhizopterin, aporhizopterin, vitamin B_c (*98*), pilocarpine (*64*), and benzothiomorpholine (*117*) have been studied at the dropping mercury electrode. Vitamin B_1 and pilocarpine give catalytic hydrogen waves. The data reported for the other compounds is insufficient to determine the exact nature of the reduction.

Determination of Metals. The polarographic determination of organic compounds can be used indirectly to determine inorganic ions. The procedure consists of adding a known amount of a polarographically reducible reagent to precipitate the ion and then without filtering the precipitate, determining the amount of organic reagent in solution. This variation has been used to determine Mg^{++} by 8-hydroxyquinoline (*118*) and Ca^{++} by means of picrolonic acid (*33*). The method may be used likewise to determine organic substances by precipitating the compound with inorganic ions and determining the excess of metallic ions present. This procedure has been used to determine soap by precipitating with excess cadmium sulfate (*40*).

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AMPEROMETRIC TITRATIONS

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TITRATIONS based on the measurement of polarographic diffusion currents were first performed by Heyrovský and Berezicky (*9*), who used the term "polarographic titration" for the new technique. Majer (*41*) simplified the technique by measuring diffusion currents at a constant applied e.m.f. rather than by recording a series of polarograms, and proposed the name "polarometric titration." Kolthoff and Pan (*26*) suggested the name "amperometric titration" as more consistent with the terminology applied to other electrometric titrations—viz., potentiometric and conductometric. While the name "amperometric" may be criticized on the basis that it emphasizes the unit of measurement rather than the quantity measured, it is a more descriptive name and is widely used.

In a strict sense, the term amperometric should be applied only to titrations in which a diffusion-controlled limiting current is measured, to differentiate it from methods such as the "dead-stop" end point of Foulk and Bawden (*7*), or the "galvanometric" titration of Salomon (*47*) in which the end point is detected by the sudden polarization or depolarization of electrode systems.

The principles of this method have been described by several investigators (*11, 16, 21, 54*); hence in the present review the emphasis is placed on the advantages and limitations of the method as well as on a critical evaluation of recent applications.

TITRATIONS WITH DROPPING MERCURY ELECTRODE

The dropping mercury electrode in principle can be applied to a wide variety of titrations, because any polarographic electrode reaction potentially can serve as the indicator electrode reaction. Considering the fact that only one of the two reactants in the titration needs to yield a polarographic diffusion current, the scope of possible titration reactions includes those which can serve for indirect polarographic analyses. For example, sulfate ion yields no polarographic diffusion current, but the addition of a known excess of lead ion renders possible the indirect determination of sulfate, while the detection of the lead diffusion current after the end point serves as the basis of an amperometric titration (*27, 41*).

Comparing the amperometric titration with direct or indirect polarographic determination, the titration procedure possesses certain advantages. It is unnecessary to maintain close temperature control in titrations, as long as the temperature does not vary appreciably during the titration. Comparisons can be made directly on titrations carried out with any capillary without calibration. In cases involving precipitates of moderate solubility, the extrapolation of a titration curve removes the uncertainty of the contribution of the precipitate to the measured current. Titrations can often be carried out with greater accuracy than direct measurements, especially in dealing with moderately concentrated solutions which would have to be diluted for polarographic measurements. The apparatus may be simplified greatly for routine work (*6, 54*). A simple voltage divider to provide 0.1-volt increments of applied e.m.f. and a sensitive galvanometer with a suitable shunt are sufficient. The use of an externally applied e.m.f. can often be avoided entirely by preparing a reference electrode of suitable potential, and short-circuiting the reference electrode–dropping electrode system through a shunted galvanometer (*15*). A microammeter is suitable for current measurements if a condenser circuit is included for damping the oscillation of the current (*40, 46, 53*). Titration cells are described by Langer (*36*) and by Stock (*5, 52, 54*).

In comparison with other electrometric titrations, the amperometric titration potentially possesses wider scope. Many substances which are not potential-determining in solution yield irreversible polarographic waves with well-defined diffusion current regions. This is especially true of organic substances such as aldehydes and ketones, peroxides, and nitro compounds, as well as many inorganic materials. The high hydrogen overvoltage of mercury permits its application at very negative potentials. The formation of amalgams permits the deposition of certain metals—e.g., alkali metals—on mercury in cases where they would be unstable in the presence of water. Applications in the region of positive potentials are limited by the electro-oxidation of mercury.

Amperometric titrations are especially suited for the titration of dilute solutions. A concentration range of 0.01 to 0.001 N is ideal.

The main theoretical disadvantage of the amperometric titration is that the presence of large amounts of materials (electrolytes or nonelectrolytes), yielding polarographic diffusion currents at lower potentials than that used for the titration, must be avoided. By changing the potential at which the titration is performed, it is sometimes possible to avoid interferences. For example, the titration of lead with dichromate (*26*) at a potential of -1.0 volt (*vs.* the saturated calomel electrode) gives a V-shaped curve because both lead and dichromate ions are reducible at this potential. By performing the titration at zero potential, an inverted L-shaped curve results because lead ions are not reducible at the applied potential. Either titration yields satisfactory results, but by using the lower potential, the interference of substances of intermediate reduction potential is avoided. Thus dissolved oxygen interferes in the first case, but not the second.

A practical disadvantage is that in most cases dissolved oxygen must be avoided or removed. Some investigators prefer to use air-free reagents, to use inert gases to remove air from the sample, and to stir the solution between measurements. Most titrations are carried out by passing nitrogen through the cell for a few minutes after each addition, and then shutting off the gas stream during the measurement. In this connection, the apparatus designs of Wise (*58*) and of Laitinen, Higuchi, and Czuha (*29*) are of interest in permitting the continuous passage of gas during measurements.

Often a practical limitation is the rate at which reaction equilibrium is reached during the titration. This is especially true of titrations involving organic reagents. In situations where several minutes of waiting are necessary before equilibrium is reached even with an excess of reagent, an indirect polarographic determination of the excess reagent is to be preferred.

In precipitation reaction, a limiting concentration is reached when the precipitate, owing to its solubility, produces a diffusion current which is the same order of magnitude as that given by a moderate excess of reagent. Langer and Stevenson (*37*) have described a graphical method of locating the end point which is valid, providing that solubility equilibrium is reached at each titration point in the vicinity of the end point. Kolthoff and Laitinen (*17*) have calculated the location of the minimum in V-shaped titration curves in relation to the equivalence point.

TITRATIONS WITH ROTATING PLATINUM ELECTRODES

The advantages to be sought in applying the rotating platinum electrode rather than the dropping mercury electrode are increased sensitivity and greater simplicity and convenience.

Increased sensitivity is brought about by increasing the rate of diffusion by stirring. A hundredfold or greater increase in diffusion current over the dropping mercury electrode can be achieved in favorable cases. The absence of a "condenser current" decreases very markedly the residual current, thus permitting the use of sensitive current-reading instruments.

The fact that the diffusion current is steady rather than fluctuating is an obvious advantage in simplicity of measurement. Because of the inertness of platinum anodes, a much wider range of positive potentials can be used. Thus many titrations can be carried out in the region of potentials at which dissolved oxygen does not interfere. Such titrations can be carried out in open beakers rather than in closed systems.

However, the possible scope of amperometric titrations with the rotating platinum electrode is much narrower than with the dropping mercury electrode. First, many potential determining systems yield highly irreversible current-voltage curves at rotating electrodes. For example, dichromate does not yield a cathodic diffusion current (*22*). Secondly, the low hydrogen overvoltage of platinum is a limitation in the range of negative electrode potentials. This disadvantage might be overcome by plating with a suitable high overvoltage metal. Thirdly, the difficult technique of titration in oxygen-free systems using a rotating electrode has limited the practical applications to cases in which oxygen does not interfere. Fourthly, the electrode surface is not renewed continually during operation. Hence the behavior of a solid electrode may depend somewhat upon its previous history. The use of surfaces other than platinum may require cumbersome operations between titrations.

In spite of these limitations, it may be said in general that if a given titration can be performed with both the dropping mercury electrode and the rotating platinum electrode, the latter is preferable for routine work.

APPLICATIONS OF DROPPING MERCURY ELECTRODE

The volumetric determination of sulfate is a problem of considerable practical importance. Barium would be the ideal precipitant on the basis of solubility, but the lack of suitable indicator electrodes has prevented the development of a satisfactory potentiometric method. The conductometric titration is not applicable in the presence of high concentrations of foreign electrolytes. Consequently, the amperometric determination has aroused considerable interest. The early work of Heyrovský and Berezicky (*9*) was based on precipitation with barium ion, but the method is subject to severe limitations because of interference by substances of lower half-wave potential than the barium ion. The lead ion is ideal as a precipitant from the viewpoint of polarographic convenience, the main disadvantage being the appreciable solubility of lead sulfate. Majer (*41*) described a graphical method of locating the end point. This method was criticized by Kolthoff and Pan (*27*), who pointed out that a knowledge of the solubility of lead sulfate in the titration medium would be required, and that the method is of limited practical utility because of the great variation of solubility with ionic strength. They emphasized the advantage of the extrapolation method of locating end points, and made a systematic study of the accuracy of the titration. In 0.01 M solution, sulfate can be titrated with a precision and accuracy of 0.2%.

Spalenka (*50*) suggested the addition of alcohol to suppress the solubility of lead sulfate. Kolthoff and Pan (*27*) recommended 20 to 30% ethanol as a titration medium, and reported an accuracy of $\pm 0.3\%$ for 0.001 M sulfate in 30% ethanol. High results (1 to 2%) were observed in the presence of 0.01 to 0.05 M potassium nitrate. The error was attributed to coprecipitation of lead nitrate. High concentrations of potassium ion lead to low results owing to the formation of a double salt, $PbSO_4.K_2SO_4$. Applications of the method to the determination of sulfur in coke (*1*) and of sulfate in precipitated alumina (*4*) have been described.

Lead ion has been studied as a precipitant for a number of other anions. Kolthoff and Pan (*27*) described the titration of oxalate and ferrocyanide with lead. Oxalate was titrated without the addition of alcohol with an accuracy of 0.2% in 0.01 M solution and 0.5% in 0.001 M solution. Ferrocyanide gave an end point corresponding to the formation of lead ferrocyanide. The titration of chloride with lead in alcohol-water medium (*28*) appears to have no advantage over silver or mercurous ion as precipitants. The titration of molybdate with lead was suggested by Thanheiser and Willems (*56*) as a method for the determination of molybdenum in steels. A prior separation of iron and of tungsten is necessary. The titration was carried out under conditions such that the lead ion gave a diffusion current whereas the molybdate was not reduced.

The titration of lead ion with dichromate has been thoroughly investigated by Kolthoff and Pan (*26*), who obtained excellent results in acid solution using a potential of −1.0 volt (*vs.* the saturated calomel electrode) where both reagents yield diffusion currents. An accuracy of 0.2% was achieved in the titration of 0.01 *M* lead solution. To avoid the interference of reducible materials such as oxygen and to simplify the apparatus, titrations were also carried out at a potential of 0.0 volt (*vs.* the saturated calomel electrode) by short-circuiting the titration cell through a shunted galvanometer. Under these conditions, the diffusion current of lead was not observed, and an "inverted L" type of curve resulted. Again, excellent results were observed in acid solution, even for 0.001 *M* lead. In neutral solution, low results due to the formation of basic salts were observed. An attempt was made to determine both lead and barium in a single titration. Serious coprecipitation of barium chromate with lead chromate prevented titration in neutral solution. In acid solution, barium chromate is soluble and does not interfere with the determination of lead.

Kolthoff and Gregor (*14*) studied the titration of barium with chromate at an applied potential of −1.4 volts. In aqueous medium, the formation of supersaturated solutions caused a very slow attainment of equilibrium in dilute (0.001 *M*) solution. Titrations in 20 to 50% ethanol were successful in that solubility equilibrium was rapidly reached, but the results were 2.4 to 5% low. The error was attributed to coprecipitation of barium salts with barium chromate or possibly the formation of basic barium chromate.

The titration of fluoride with thorium or lanthanum nitrate was studied by Langer (*34*), who stated that the current passing after the end point at a potential of −1.7 volts (*vs.* S.C.E.) is caused by the reduction of nitrate in the presence of thorium or lanthanum. Kolthoff and Lingane (*21*) criticized the interpretation of the cause of the current and suggested the need for further investigation. Langer reported satisfactory results with fluoride concentrations as low as 2×10^{-4} molar. The same interferences were noted as in the usual sodium alizarin sulfonate titration, and therefore a prior distillation is necessary. A careful adjustment of pH to a value between 6 and 8 was recommended. The results suggest that the current may be due to hydrogen ion produced by hydrolysis of thorium or lanthanum ions, and that some attention should be paid to the buffer capacity of the solution. The effect of alcohol is peculiar in shifting the end point to considerably higher values. In its present state of development, the amperometric fluoride titration appears to possess little advantage over the indicator method.

Spalenka (*50*) titrated ferrocyanide with zinc at a potential of −1.2 volts, measuring the diffusion current of zinc. The best results were obtained in 0.2 *N* hydrochloric acid solution. A noticeable slowness of precipitation of $K_2Zn_3[Fe(CN)_6]_2$ was reported at room temperature; at 50° C. the precipitate formed more rapidly, but the accuracy was not affected. In ammoniacal medium the solubility was repressed, but reproducible results could not be achieved.

Neuberger (*45*, *46*) titrated phosphate with bismuth oxyperchlorate, determining the bismuth diffusion current. The method is of limited utility because it is applicable only to relatively concentrated phosphate solutions (above 0.035 *M*) and because all anions except perchlorate must be absent because they form complexes with bismethyl ion (*13*). Kolthoff and Cohn (*13*) described a titration of phosphate with uranyl acetate in the presence of potassium chloride to form UO_2KPO_4, detecting the end point by the diffusion current of uranyl ion in acetic acid medium. They recommend the destruction of organic anions by ignition or by oxidation with sulfuric and nitric acids to prevent interference caused by the formation of uranyl complexes. Adjustment of the acidity is important in regulating the speed of formation of the precipitate.

The titration is carried out in 20% ethanol, and the concentration of phosphate is limited to less than 0.01 *M*. Moderate amounts of magnesium, barium, and calcium cause no interference. The precipitation of calcium sulfate in the 20% ethanol medium caused an error due to coprecipitation of phosphate. Hence the concentration of calcium and sulfate in the final solution should not exceed 0.02 *M* and 0.01 *M*, respectively. With the recommended procedure, an accuracy of 1% or better was obtained in solutions 0.01 to 0.0003 *M* in phosphate. Alkaline earth phosphates can be titrated by the standard procedure. Iron interferes, but it can be removed by the addition of cupferron followed by ether extraction. Indirect polarographic determinations of phosphate based upon the determination of excess molybdate have been described by Uhl (*57*) and by Stern (*51*).

Amperometric titration of chloride with mercurous ion (*21*) and with silver (*20*, *42*), and of iodide with mercuric ion (*21*) using the dropping mercury electrode have been described. As halide titrations can be more conveniently carried out with a rotating platinum electrode, no details are given here.

Titrations of titanous chloride with several oxidizing agents were described in the early work of Strubl (*55*) and Spalenka (*50*). In the presence of tartrate or citrate, the titanous-titanic system yields a smooth composite anodic-cathodic wave. Using an oxidizing agent such as ferric iron, ferricyanide, chromate, bromate, or iodate, the anodic current of the titanous titanium decreases to zero and changes sign upon addition of excess oxidizing agent. Although Spalenka (*50*) stated that the titration points in the vicinity of the end point lie on the same straight line, Kolthoff and Lingane (*21*) point out that this could not be generally true.

An interesting type of amperometric titration is that based upon compensation of the anodic current of one substance by the cathodic current of another, even though a direct reaction between the two substances may not be involved. Thus Kolthoff and Miller (*24*) titrated oxygen, which yields a cathodic wave (*25*), with sulfide ion which yields an anodic diffusion current due to the formation of mercuric sulfide at the dropping electrode. No simple stoichiometric ratio of the two substances exists at the end point, but rather the quantity $nCD^{1/2}$ becomes equal, where n is the number of electrons involved per molecule in the electrode reaction, C is the concentration, and D is the diffusion coefficient.

Another example of an amperometric titration involving the compensation of current is the titration of stannous tartrate, which yields an anodic diffusion current at a potential of −0.2 volt (*vs.* S.C.E.), with cupric ions, which gives a cathodic current at the same potential. Lingane (*39*) showed that no direct reaction occurs in the bulk of the solution.

Organic reagents have successfully been used in several amperometric titrations. Advantages to be sought are high selectivity and high sensitivity. Many organic analytical reagents have polarographically reducible functional groups and potentially are useful for the determination of substances that cannot be directly determined by polarographic means.

Kolthoff and Langer (*18*) have titrated nickel in ammoniacal solution with dimethylglyoxime at a potential of −1.85 volts (*vs.* S.C.E.) when both nickel and reagent show diffusion currents. An accuracy and precision of 0.4% in 0.01 to 0.001 *M* solution was achieved. At a concentration of 0.0001 *M*, the results were still accurate to within 2%. Cobalt was found to interfere because of the formation of a soluble and reducible complex. A prior separation of cobalt as potassium cobaltinitrite was recommended in cases where the cobalt content was more than 5% of the nickel content.

The titration of cobalt, copper, and palladium with α-nitroso-β-naphthol was studied by Kolthoff and Langer (*19*). At potentials more negative than −0.6 volt, the reagent yields a diffusion current both in acid and in ammoniacal medium. For cobalt, an acetate buffer was recommended, using an applied potential of

-0.6 volt. Under these conditions, the cobalt derivative is stable toward air oxidation, and only the reagent gives a diffusion current. Copper and palladium can be titrated in the same way but here the metal ion also yields its diffusion current. One cobalt ion combines with four molecules of reagent, whereas one copper or palladium ion combines with two molecules. Zinc, aluminum, and manganese were found not to interfere. Results were high in the presence of nickel. Further work is needed to establish the scope of the reagent and to investigate interferences in more detail.

Langer (*35*) showed that α-benzoin oxime can be used for the titration of copper. At applied potentials between -0.8 and -1.4 volts, using an ammoniacal medium, the reagent was not reducible and L-shaped titration curves were observed. At -1.7 volts, a V-shaped curve was observed, because both reactants are reducible. The solubility of the precipitate increases with increasing ammonia concentration. For 0.001 *M* copper solution in 0.02 *M* ammonium hydroxide solution, the results were accurate to about ±1%. Nickel was found to interfere badly. Iron, lead, and zinc showed smaller interferences. A more detailed study of the effect of foreign ions should be made.

Neuberger (*45*) proposed the determination of copper with salicylaldoxime. An excess of reagent was added and titrated with a standard copper solution, and the appearance of the copper diffusion current was noted.

Stock (*54*) investigated the reaction between quinaldic acid and copper in acetate buffers, and showed that equilibrium is reached more rapidly if the copper solution is added to the quinaldic acid solution than if the procedure is reversed. Accordingly, the recommended procedure is to add an excess of quinaldic acid and back-titrate with copper.

Bismuth has been titrated with 8-hydroxyquinoline (*8*), using a tartrate solution with an acetate buffer added. At an applied e.m.f. of 0.85 volt, both reactants yield diffusion currents. The same reagent has been used for zinc, copper, and aluminum (*59*), in a buffered acetate medium. Magnesium was determined in an ammoniacal medium containing ammonium chloride (*59*).

The titration of potassium with dipicrylamine in cooled solutions was mentioned by Langer and Stevenson (*37*), but no details were given.

Cohn and Kolthoff (*2*) devised an indirect amperometric determination of calcium, based upon precipitation with picrolonic acid and back-titration of the excess reagent with methylene blue. The end point was detected by measurement of the diffusion current corresponding to the reduction of methylene blue to leucomethylene blue.

Another titration involving two organic substances was described by Conn (*3*). Various diamidines were titrated with sodium alizarin sulfonate to give insoluble alizarin sulfonates, the excess reagent yielding a diffusion current. The results in general were reproducible and accurate within ±0.5%.

The amperometric titration of α-tocopherol with auric chloride was studied by Smith, Kolthoff, and Spillane (*49*). In a benzoate buffer, at a potential of -0.075 volt (*vs.* S.C.E.), only the reagent gave a diffusion current. In a concentration range between 1×10^{-3} and 3×10^{-4} *M*, an accuracy of 0.3% was achieved.

Recently cupferron as a titration reagent has been studied by Kolthoff and Liberti (*38*). Accurate results were obtained in the titration of copper in neutral or slightly acid media. Equilibrium was rapidly reached. Using citrate or tartrate buffers of pH between 1 and 3, ferric iron was successfully titrated. A serious disadvantage of cupferron is its instability, which makes necessary frequent standardizations.

Kolthoff and Johnson (*10*) have recently studied *n*-nitrophenylarsonic acid as a reagent for uranyl, thorium, zirconium, titanium (IV), and tin (IV). Under carefully controlled conditions, satisfactory results were obtained for uranyl and thorium ions, with rapid establishment of equilibrium. Zirconium yielded a precipitate of somewhat variable composition. Tin (IV) gave a slow reaction. Titanium (IV) did not give a precipitate of stoichiometric composition. Tetraphenylarsonium chloride proved to be an excellent reagent for tin (IV) as chlorostannate in media of high acidity and high chloride ion concentration. Other titrations with the reagent are being investigated.

APPLICATIONS OF ROTATING PLATINUM ELECTRODE

In the early work of Nernst and Merriam (*44*) it was shown that distinct diffusion currents could be observed with a rotating platinum microelectrode for solutions of iodine, bromine, chlorine, silver ions, and permanganate ions in the presence of an excess of indifferent electrolyte. Although such diffusion currents are seldom useful for direct measurements of concentration except under carefully controlled conditions (*33*), they form the basis of several amperometric titrations.

The titration of arsenite with bromate was studied by Laitinen and Kolthoff (*33*). In an acid solution containing bromide, the end point was detected by measuring the diffusion current of bromine which was formed after the end point. Rapid and accurate titrations were carried out in an open beaker with an applied potential of $+0.2$ volt (*vs.* S.C.E.), where oxygen does not interfere. Solutions 0.001 *N* in arsenite were titrated with an accuracy of 0.1%, and 0.0001 *N* solution yielded results accurate to 0.3%. Myers and Swift (*43*) used the diffusion current of bromine to detect the coulometric end point of the same titration reaction. By using a larger electrode in a stirred solution, the sensitivity was increased considerably. A diffusion current of 1.0 microampere per 10^{-7} mole of bromine per liter was reported. In a titration volume of 50 ml., an average absolute error of 0.5 microgram of arsenic was observed regardless of the amount of arsenic being determined. The same end point was used by Sease, Niemann, and Swift (*48*) in the determination of thiodiglycol by means of electrolytically generated bromine, and by Kolthoff and Bovey (*12*) in the amperometric titration of styrene with potassium bromate. In the latter titration, using a solvent of 75% methanol and a temperature of 10° C. to minimize loss due to volatilization of styrene, slightly low but satisfactory results were obtained.

Chloride, bromide, and iodide were titrated with silver nitrate by Laitinen, Jennings, and Parks (*30*). For the titration of chloride, acetone was added to decrease the solubility, and gelatin was added to prevent depolarization by colloidal silver chloride. The titrations could be carried out rapidly and conveniently. Although accurate in 0.1 *N* solution, the titration showed a tendency toward low results at high dilution. Standardization in a similar concentration range is recommended. The successive titration of all three halides (*31*) in one solution proved to be simple, rapid, and convenient. Ammonia was added for the iodide titration, excess nitric acid for the bromide titration, and gelatin for the chloride titration. The three titrations could be carried out within 10 minutes.

Silver nitrate was used as the reagent for amperometric titrations of mercaptans (thiols) in alcoholic ammoniacal medium by Kolthoff and Harris (*15*). Amounts of mercaptan sulfur as small as 0.2 mg. in 100 ml. could be determined with an accuracy of 1 to 2%. Amounts greater than 2 mg. per 100 ml. were determined with a precision and accuracy of at least 0.3%. The mercaptan titration has been used in the determination of disulfides (*23*).

The titration of cyanide with silver (*32*) proved to be as accurate as the potentiometric or visual indicator methods in 0.2 *N* to 0.002 *N* solution, and applicable at much higher dilution. Even in 4×10^{-6} *N* cyanide, a distinct amperometric end point could be observed.

Dichromate has been titrated in acid solution with ferrous iron (*22*) using the anodic diffusion current of ferrous iron to determine the end point. Dichromate gives no cathodic current. Excellent results were found in solutions as dilute as 10^{-4} M in dichromate.

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ELECTROANALYSIS

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Although 20 years ago a foreign worker in the field of electroanalysis concluded that it "now belongs to the museum class" (*20*), the past pentad has seen a stir of activity that presages a renaissance. This worker might have been warned by the conclusion in 1883 that the work on electroanalysis was finished with the publication of Classen's classical treatise (*60*). However, the volume of current papers appearing in the field of electroanalysis is a very poor indication of the potential value of work in this field. The development of new techniques in the field of instrumentation and the re-examination of poorly founded conclusions provide opportunity for fruitful investigation.

Recent years have recorded the passing of Henry J. S. Sand (*55*), a pioneer in the development of electroanalysis, at a time when his most important work on electrodeposition with controlled cathode potential is just coming to be generally appreciated and used. In fact, the application and extension of these principles are probably the most important phase of current activities in electroanalysis.

Most developments of theoretical interest to electroanalysis are at present occurring in the field of polarographic analysis, which is treated in a separate review.

BOOKS

After 24 years a completely revised third edition of the classical Fischer-Schleicher "Elektroanalytische Schnellmethoden" has made its appearance (*56*). The length of the book has been halved from the previous edition, probably because of material shortages, but much new material relating to internal electrolysis has been introduced. This feature is likewise a reflection of war economy, as the use of internal electrolytic methods permits the substitution of base metals for platinum anodes. Material omitted from this edition of the book includes detailed description of specific procedures for the analysis of commercial alloys completely by electroanalytical methods, and the historical section included in earlier editions. Diehl has contributed another welcome book in the field of electroanalysis, a monograph on the use of the graded cathode potential control (*15*). Although the book is concerned largely with its author's own automatic apparatus for this type of analysis, other equipment is described by reference, the theory of the method is discussed, and a number of interesting and suggestive examples are presented for the practical use of this method. The only other books to appear during the years covered by this review are by Jílek (*29*), which appears to be in the possession of only a single library in the United States, and by Tamburrini (*66*) not located here at all. Neither was available to this reviewer.

REVIEW ARTICLES

In the present review there is no discussion of microelectrolysis, largely because there is no sharp differentiation of technique, de-

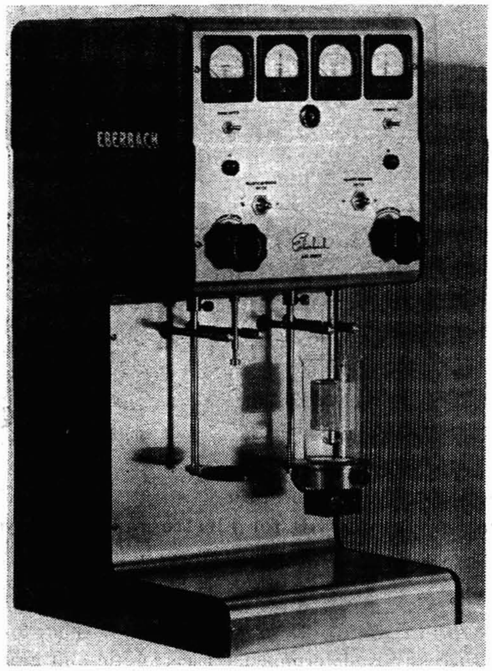

Figure 1. Self-Contained Unit for Electroanalysis

Arthur H. Thomas Co., Philadelphia, Pa.

pending on the size of the sample and the quantity of matter being determined. Trace analysis is often discussed as part of microelectrolysis, but for similar reasons is not separately treated here. Lindsey (*34*) and Sand (*54*) have published reviews covering fairly thoroughly both of these aspects of electroanalysis. Ingram (*28*) has treated both microelectrolysis and electrographic analysis in an elementary review of microchemistry. A general description of the possibilities of electrographic methods has been given by Arnold (*3*). The work of Glazunov, the inventor of the technique, has been made the subject of an article by Jirkovský (*30*).

The growing recognition of the importance of internal electrolysis becomes clear from the attention it has received from reviewers. One of the best articles is by Schleicher (*59*). Reviews of a more general character have been published by Fife (*18*), who emphasizes its use as a semimicromethod, and by Davies (*14*), who points out its value in the industrial laboratory. Guzman and collaborators have published a large number of papers concerned with means of circumventing the use of platinum electrodes in electroanalytical determinations. This work has been reviewed and summarized by Celsi (*11*).

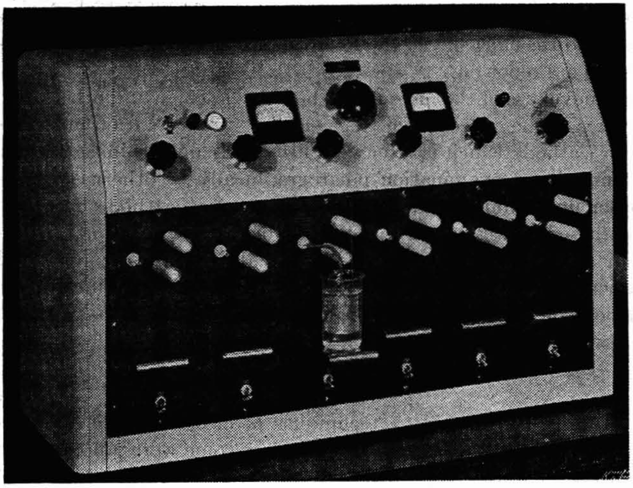

Figure 2. Self-Contained Cenco Electroanalyzer with Air Stirring

Central Scientific Co., Chicago, Ill.

A brief account of some important developments in electroanalysis, which came out of the work of the Manhattan District Project, is given by Furman (*19*).

A sketchy report of a review by Lingane on the applications of controlled potential electrolysis has also appeared (*40a*). A more detailed review of the same author's work was published early in 1947 (*36*).

EQUIPMENT

The manufacturers to whom the chemist is indebted for help have been busy with improvements on apparatus for electroanalysis. The Arthur H. Thomas Company, Philadelphia, and the Central Scientific Company and E. H. Sargent and Company, both of Chicago, have offered redesigned equipment for quantitative electrolytic depositions (Figures 1, 2, and 3). New equipment for electrographic analysis has appeared. The Arthur H. Thomas Company features a portable kit containing reagents, paper, power source, etc., necessary for work either in the laboratory or the field (Figure 4). The Fisher Scientific Company offers heavier equipment suitable for either process control or laboratory investigations (Figure 5).

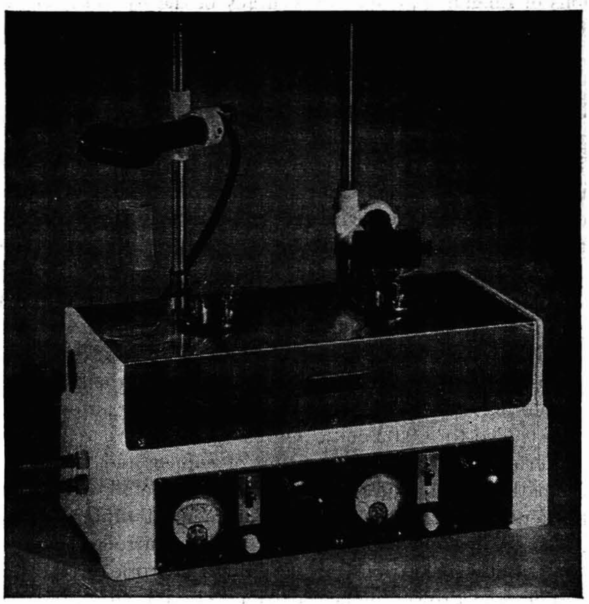

Figure 3. High-Speed Heavy-Duty Water-Cooled Electrolytic Analyzer with Magnetic Stirring

E. H. Sargent Co., Chicago, Ill.

Most of the power sources described for electroanalysis have been designed for the automatic control of the cathode potential. Two articles describe devices which activate mechanical rheostats for controlling the power delivered to the electrolytic cell. The same equipment described by Caldwell (*10*) and Diehl (*15*) acts in only one direction to decrease the power supplied to the cell. The somewhat simpler apparatus described by Lingane (*38*) acts in either direction to raise or lower the current to the cell as may be necessary. An automatic apparatus in use at the National Bureau of Standards for the same purpose but with no moving parts, neither relay nor rheostat, whose operation depends entirely on a vacuum tube circuit to control the power supply, has been briefly described with a promise of further details to come (*2*). The design of a power source for the peculiar requirements of Trishin's electrochronometric method of analysis has also been published (*68*).

Much promise for future progress in electroanalysis lies in the redesign of cells and electrodes. An interesting original design for a combined mercury cathode and anode which permit high current density and convenient handling and washing is shown in an article by Johnson (*31*). Rabbitts (*51*) reports a more conventional type of mercury cathode which he claims is faster than others commonly used. Athough time for an electrolysis is mentioned, the size of the sample being treated is not; hence comparisons cannot be made. Efforts to find means of using cheaper electrodes than platimum have been summarized by Celsi (*11*), and have also been responsible for the interest in internal electrolysis (*58*).

Lindsey (*35*) describes a silver chloride reference electrode of simple design for use in controlled cathode potential electroanalysis.

Stirring by the use of a magnetic field from a solenoid is a feature of the E. H. Sargent equipment shown in Figure 3. Webb (*70*) has suggested the use of powerful permanent magnets to accomplish this purpose. Here indeed seems to be an opportunity to combine cell, electrodes, and magnetic field in an efficient arrangement.

It is occasionally necessary for the electroanalyst to make use of a chemical coulometer, particularly in research work on analytical methods. Note should therefore be taken of a convenient coulometer described by Abers (*1*) and the investigations of Lingane (*40*) on the accuracy of the hydrogen-oxygen coulometer.

ELECTRODEPOSITION

Attention is being given to the important field of electrodeposition at a controlled potential. The development of automatic equipment for making such determinations, which seems to be a peculiarly American contribution, guarantees that a method known since about 1906 will now come into more general use, particularly in industrial laboratories. A book (*15*) and review (*40a*) treat current applications. Lingane (*39*) has described a method for the determination of copper in copper-base and tin alloys in which relatively large amounts of tin, antimony, lead, and zinc do not interfere. Small amounts of iron, nickel, arsenic, and phosphorus may also be present. Deposition is from a tartrate solution with the potential at the cathode automatically (*38*) controlled to ±0.02 volt. Only about 1 hour is required for the determination. The separation of copper and tin by controlled cathode techniques has been studied in detail by Diehl and co-workers (*16*) with equipment of somewhat different design (*10, 15*). A new development in the use of controlled potentials for electrolytic separations, an outgrowth of work for the Manhattan District Project, is the use of a potential buffering solution, to date only briefly reported by Furman (*19, 21*). By controlling the total concentration of uranium, the deposition of chromium, molybdenum, manganese, and other elements may be prevented when electrolysis with a mercury cathode is used for purposes of separation. An equilibrium between U(III) and U(IV) limits the decomposition potential at the cathode.

Electroanalysis has been as valuable to the analyst for the separations in analysis that it makes possible as for the actual determinations by electrolytic deposition. In the analysis of copper-base alloys, the removal of copper, lead, etc., is necessary as a preliminary to the determination of minor constituents. Zischkau (*73*) employs electrolysis to remove the base metal from copper alloys before applying colorimetric methods. Goodman (*23*) uses a similar technique preliminary to the determination of iron with *o*-phenanthroline, by a colorimetric procedure. In a paper with a bibliography of over 200 references, Hammond (*25*) has reviewed the methods for the separation of cadmium from zinc and finds that electroanalysis at a controlled potential has many advantages. He describes a method for the analysis of a low melting silver solder in which silver, copper, cadmium, and zinc are successively determined. Electrolytic and gravimetric methods for the separation of cobalt and nickel have been compared by Nenadkevich (*46*) who finds that the nickel cyanide complex is more susceptible to decomposition at the anode than a cobalt complex in the same solution. By electrolysis the nickel is precipitated at the anode as a black oxide which may be filtered off when the electrolysis is complete and weighed after ignition in a platinum dish.

Figure 4. Portable Kit for Electrographic Analysis

Arthur H. Thomas Co., Philadelphia, Pa.

Tucker (*69*) has re-examined classical conclusions about conditions for the separation by electrolysis of manganese and lead. In his preliminary report he finds that, contrary to what one would anticipate from unsubstantiated statements in the literature, at least 60 mg. of lead can be almost quantitatively separated from an equal weight of manganese under conditions easy to achieve. An interesting combination of electroanalysis with closely related polarographic analysis has been demonstrated by Lingane (*37*). Metals are separated by deposition in a mercury cathode, and a feature of this technique is that the optimum values of the cathode potential can be directly derived from the polarograms for the solution. A mercury cathode of special design (*31*) has also been advantageously used for the removal of interfering elements prior to polarographic and other determinations of aluminum, alkaline earth, and alkali metals by Parks and co-workers (*48*). Observations on the relationships between electrode spacing, area of the cathode, and current density and the efficiency of the removal of constituents from the solution are reported.

A novel use of the mercury cathode by Furman and others (*21*) relates to the collection of trace elements from solution in a mercury cathode which is later volatilized, leaving behind a residue of metals for examination polarographically or otherwise. Another important phenomenon of the mercury cathode described by these investigators is the lowering of the overvoltage of hydrogen on the cathode after traces of platinum, iron, copper, and other metals have been deposited in it, causing incomplete deposition of trace elements from solution.

INTERNAL ELECTROLYSIS

Although many of the techniques of electroanalysis were invented when the science was still young, some were not exploited until comparatively recent years. Internal electrolysis is one of these. This subject has been developing steadily as a semimicro or perhaps more properly a trace method of analysis, stimulated by the growing recognition in metallurgy of the importance of small concentrations of alloying elements or impurities (*14, 18, 59*). The only systematic investigation during the period of this review was made by Schleicher, who is most concerned with the feature of internal electrolysis that permits the elimination of a platinum anode. Schleicher (*59*) studied the conditions of temperature, stirring, position of the anode, etc. which affect the deposition of copper by internal electrolysis. Subsequently (*57*) he examined methods for the determination of lead, nickel, cobalt, tin, and antimony by internal electrolysis, but under the conditions studied the determination of antimony was not successful. The separation of cobalt and nickel was also not possible. Details are given in a third paper (*58*) for the separation and determination of copper from commercial products, especially alloys. The determination of copper in aluminum alloys has been reported by Suvorovskaya (*64*), who employs an aluminum anode.

COULOMETRY

Most methods of electroanalysis have depended on the power of the electric current to precipitate an element or its compound from solution. The equivalence of the amount of an element precipitated with the amount of electricity expended, known as Faraday's law, provides another means for the quantitative estimation of an element and can be applied in a number of ways. Zakhar'evskiĭ in 1938 (*72*) published one of the earliest applications of this principle when he determined lead and copper by depositing them from a solution and then measuring the current they generated as they redissolved. The same year Szebellédy (*65*), using a platinum cathode and silver anode, was able to standardize, by electrolyzing at constant current and under conditions which produced a 100% current yield, a number of relatively pure solutions with considerable precision. One of the most interesting applications of Faraday's law has been made by Lingane (*40*). Employing cathode potential control, a mercury cathode, a silver anode, and a hydrogen-oxygen gas coulometer to measure current, he demonstrated the successive determination of copper and bismuth, which would have been difficult to accomplish by classical procedures in electroanalysis. Lead was also determined with satisfactory precision. Another feature of this important paper was the demonstration that although their reduction potentials are separated by only 0.20 volt, lead and cadmium can be separated by this method. Half-wave potentials derived from polarographic analyses can be used directly, as mercury is used as cathode. Trishin (*67*) also uses a mercury cathode for the method which he styles "electrochronometric analysis" because time is the variable measured for the deposition of an element at constant current. The cell of his apparatus is divided to prevent reoxidation of the catholyte at the anode. An automaton (*68*) is used to control and record the current. Zinc and copper are successively determined on the same solution in the absence of other ions. It is apparent from Lingane's and Trishin's work that coulometric methods lend themselves to instrumentation and automatic operation.

Figure 5. Electrograph

Fisher Scientific Co., Pittsburgh, Pa.

This is further apparent in a somewhat different type of application in which a titrating agent has been generated in stoichiometrical quantities by the use of measured quantities of electricity, and the titration may be automatically interrupted at the end point. Epstein (*17*) electrolyzes sodium bromide solution in a divided cell to produce minute quantities of sodium hydroxide used for the titration of small amounts of acid. A constant current is employed and the time to reach the end point is recorded with a stop watch or inscribed on a drum. The end point is observed potentiometrically. Swift (*43, 61*) and his co-workers have generated bromine electrolytically with a constant current and used it to oxidize thiodiglycol and arsenious acid. A small excess of bromine beyond the stoichiometrical amount carries the titration beyond the end point. The unused bromine is measured by observing the current between two indicating electrodes on which about 0.3 volt is impressed. This indicating current has been made the subject of an interesting study (*43*), although the details are inappropriate to this review.

ELECTROSOLUTION

The electric current has been serviceable to the analyst as a means of dissolving samples as well as for precipitating constituents. An important application of this principle has been for electrographic analysis. However, except for the reviews and new equipment previously noted, no papers have recently appeared in this field. Besson (*9*) applies a method initially developed by Rollet (*53*) to demonstrate the composition of thallic oxide (Tl_2O_3).

Metallurgists continue to make good use of the electric current for the dissolution of steel samples for the determination of nonmetallic inclusions in steel. Shapiro (*62*) and Popova (*50*) describe procedures which the abstracts available indicate to be conventional.

RECENT ELECTROANALYTICAL STUDIES BY ELEMENTS

Antimony. Schleicher has attempted unsuccessfully to determine antimony by internal electrolysis (*57*).

Arsenic. Besides the titrimetric method for the determination of arsenic as arsenious acid (*43*), the classical evolution method has been the subject of further study (*52*). Rogers compares the generation of arsine by zinc and acid with the electrolytic method using a cell of special design and a mercury cathode. He finds that the electrolytic cell is more reliable and hence to be preferred. The arsenic is actually determined by a colorimetric procedure.

Cadmium. Some causes of poor results in the electrolytic determination of cadmium from a cyanide solution are discussed by Hering (*26*), who finds that the addition of small amounts of a hydrazine salt prevents the decomposition of the electrolyte by oxidation products from the anode. Guzmán (*24*) extends his method of electrolysis with a reference electrode to the determination of cadmium, using base metal cathodes. He studied ammoniacal, ammonium formate, ammonium cyanide, ammonium oxalate, and hydrochloric acid electrolytes with platinum or passive metal anode. The review of Hammond (*25*) on the separation and determination of cadmium in the presence of zinc has been mentioned.

Cobalt. Although Schleicher (*57*) was unable to separate nickel and cobalt satisfactorily by internal electrolysis, he was able to determine cobalt in an acetate, nitrate, or chloride solution. The cobalt deposited is not contaminated either with carbon, as is so frequently the case when an outside source of power is used, or with platinum as sometimes occurs with a prolonged electrolysis when a platinum anode is used.

Copper. Copper continues to be the favored element of the analyst and electroanalyst. In a series of papers (*5–7*) Bertiaux has discussed in detail the analysis of copper-base alloys and gives procedures for the determination of tin, copper, lead, nickel, antimony, and silver by electrolysis. Babson (*4*) has discussed the determination of copper in manganese bronze, Golubtsova (*22*) in the analysis of zinc alloys, Norwitz (*47*) in the analysis of aluminum alloys, and Levine (*33*) in steel and cast iron. Martens (*42*) has contributed an interesting study on the problem of determining small amounts of copper in the presence of arsenic. The possible means of accomplishing this are studied in considerable detail, and conditions defined for obtaining accurate determinations of copper. A qualitative microscopic test for copper in reagents by electrolysis on a fine wire is described by Jung (*32*).

Gold. Electrolytic deposition of gold (*44*) on a lead cathode has been used as a preliminary separation of gold from other impurities in a method designed to give greater accuracy than customary procedures. After most of the gold has been deposited from solution, the cathode is folded and cupelled.

Lead. Lead is second only to copper in its popularity with the electroanalyst. Methods for its determination in aluminum (*47*), zinc (*22*), and copper (*4, 6, 7, 58, 59*) have appeared. Preference is almost invariably given to determination as the dioxide. Bertiaux records a table (*5*) for the variation in the conversion factor of lead dioxide to lead with the amount of lead determined. Tucker (*69*) has re-examined the determination of lead in the presence of manganese and finds that cleaner separations are possible than is generally believed. By the use of a magnesium anode Schleicher deposits lead cathodically (*57*) with success. Hertelendi (*27*) has investigated the conditions by which an anodic deposit of the lead dioxide can be converted by heat to either litharge or minium. McLean (*41*) reports an interesting method of differentiating lead under the microscope in polished metal sections by an internal electrolytic procedure. Celsi (*12*) modifies the procedure for the deposition of lead as dioxide by the addition of copper nitrate and the use of a copper cathode coated with collodion.

Nickel. Nenadkevich (*45, 46*) separates nickel from cobalt and determines the nickel by anodic precipitation from a cyanide solution as oxide. A chromate depolarizer is used to prevent cobalt and nickel from depositing at the cathode. Schleicher (*57*) has a method for depositing nickel by internal electrolysis, which is successful for nickel alone but not in the presence of cobalt.

Thallium. Both Chrétien (*13*) and Besson (*8*) find that the determination of thallium by deposition of the oxide at the anode is very unsatisfactory. However, Chrétien describes a method by which thallium may be accurately determined by deposition on an amalgamated platinum cathode from a solution containing benzoic acid. An organic agent in the solution is necessary, but of those tried benzoic acid appears best.

Tin. Tin may be quantitatively deposited by internal electrolysis from a chloride solution, according to Schleicher (*57*). Jung (*32*) describes a qualitative microtest for its detection in reagents.

Zinc. Although the determination of zinc electrolytically has never been popular because of its troublesome characteristics, recommendations for its use continue to appear in the literature. Methods for the determination of zinc in magnesium-base alloys have been described by Weinberg (*71*) and von Stein (*63*). Golubtsova (*22*) has used electrolysis to determine zinc in zinc alloys. Hammond (*25*) has described the analysis of a low melting silver solder in which silver, copper, cadmium, and zinc may be successively determined on the same cathode. A qualitative electrochemical test for zinc in reagents is described by Jung (*32*).

Patterson (*49*) determined zinc in the presence of thorium by electrolysis of an aqueous solution of the perchlorates to which sodium citrate and acetone had been added. In this way as much as 0.2 gram of zinc could be precipitated at a time.

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CHROMATOGRAPHIC SEPARATIONS

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THE interpretation of natural phenomena in terms of physics and chemistry depends upon knowledge of the properties of particular chemical substances. Because each substance must be isolated in a high state of purity before many of its physical and chemical properties can be determined, progress in the natural sciences hinges upon the development of efficient analytical methods (*10, 51*).

Of the various techniques that have been devised for the resolution of mixtures, the chromatographic adsorption analysis, first described by Tswett in 1906, is one of the most effective (*25*). Now that scientists have become aware of the wide applicability, the extreme sensitivity, and the great rapidity of this adsorption method, hundreds of new uses and numerous modifications of the procedure have been described (*147*).

From pedagogic and developmental points of view, it is significant, as related by Dhéré (*45*), that Tswett, the son of a Russian father and an Italian mother, obtained his doctorate in botany with Marc Thury at Geneva. Later, at the veterinary institute at Warsaw, this unlicensed chemist of that day observed that pigments in the extracts of green leaves form a series of green and yellow bands when a solution of the mixture is filtered through a glass tube filled with precipitated chalk. Moreover, Tswett found that complete separation of these pigments from one another could be effected only by washing the adsorbed substances with fresh solvent or with mixtures of solvents. Although adsorption columns had previously been used for the partial resolution of mixtures, this development of the chromatogram with various solvents represented a unique advance in the use of adsorption methods.

In the 45 years preceding Tswett's basic discovery, Schönbein, Goppelsroeder, and many others had observed that solutes concentrate in distinct zones as solutions are drawn into strips of filter paper by capillary action (*76, 77, 101*). But not until recently has it been realized that the principles involved in this so-called "capillary analysis" are identical with those in chromatographic analysis (*32, 117, 148*).

Viewed from the vantage point of current knowledge, many early modifications of the capillary adsorption method, such as the addition of reagents and indicators to the paper (*37, 63, 77, 98*), have been utilized in Tswett's columnar analysis. Conversely, numerous advances in the use of adsorption columns, especially the development of the chromatogram, have now proved applicable to capillary analysis (*37, 76*). In view of the similarity between these two methods, capillary analysis is frequently called "paper chromatography" and "paper partition chromatography" (*35, 37, 84, 85, 86*).

The efficiency and convenience of chromatographic separations in relation to those obtainable by other methods vary greatly with the field of investigation. Applied to some substances, such as the inorganic ions (*70, 112, 113, 132*) and the amino acids from various natural sources (*35, 36, 37, 84, 90, 115, 116*), chromatographic analysis has often contributed little more than a convenient confirmation of the results obtained by the conventional methods of analysis. In other fields, as with the polyene compounds, each new application of the chromatographic technique has revealed many new compounds that had escaped detection or isolation by other methods (*124, 149, 150*).

In the past five years, advances in chromatography have followed many courses. There have been significant improvements of the apparatus and procedure. New adsorbents, particularly the ion exchangers and the hydrated gels, have been introduced on a large scale. A variety of solvents, such as the cyclic nitrogen compounds, higher alcohols, and salt solutions, have been employed as solvents and eluants. As in the past, most studies have dealt with the resolution of mixtures, both of inorganic and of organic substances. These applications of the method have been enlarged to an industrial scale, and they have been refined to microgram proportions for qualitative and quantitative analysis. Adsorption in paper has been widely employed for the examination of biological products; a recent review contained as many as 51 references (*35*). Numerous attempts have been made to standardize the paper and the columnar methods as an aid to reproducibility, as a basis for engineering applications, and as a foundation for physical and mathematical interpretations of the process (*24, 73, 74, 107, 113, 114, 126, 128, 129, 132*). Several reviews of various aspects of the paper (*51, 77*) and columnar chromatography (*6, 29, 46, 54, 84, 85, 89, 105, 113, 132, 134, 144, 148, 151*) have treated many aspects of the subject that could not be considered here.

METHODS

Apparatus. Certain modifications of the apparatus facilitate particular applications of the chromatographic methods. Glass adsorption tubes, with a slight, uniform taper toward the base, and aluminum tubes aid the removal of the intact, cohesive mass of the adsorbent after the chromatogram has been developed (*16, 75*). A transparent plastic adsorption tube with a removable, longitudinal section permits addition of reagents to the adsorbent while it is still in place (*14, 42*). Rotating columns with a hollow center, akin to the tubular basket of a centrifugal filter partially filled with adsorbent, accelerate the flow of solvent and, therefore, the rate of the separations (*62*). Columns with removable quartz windows have also been described (*30*).

Removal of the cohesive mass of the adsorbent from the adsorption tubes, which is desirable for the detection of colorless substances with reagents, is most easily accomplished when the columns are formed from a slurry of solvent and adsorbent. When columns are packed with certain dry adsorbents, such as precipitated chalk, the slug of adsorbent can often be removed after it has been sucked free of excess solvent. But with long columns formed by pressing dry, resilient, powdered sugar or Celite into the tubes, successive portions of the adsorbent must be dug out one by one with a long spatula (*124*).

Devices for the collection and examination of successive portions of the percolate facilitate the detection of solutes as they are washed through the columns. Successive portions of the percolate may be collected and recorded automatically by gravimetric (*28, 29, 128, 129*), volumetric (*90*), and spot testing (*47*) techniques. Variable portions of the percolate may be collected without interrupting the flow of solvent or the vacuum pressure by use of the all-glass receivers designed for use in vacuum distillation (*1*). Solutes in the percolate from a column may be detected and estimated by continuous recordings of optical density or refractive index of the effluent (*3, 28, 29, 48, 90, 128, 129*).

Procedure and Objectives of Columnar Adsorption. Thanks to the studies of Tiselius and his co-workers, much basic information pertaining to the separation of mixtures has recently been obtained by the percolation of a solution through a column until the solutes appear in the percolate (*28, 29, 128, 129*). Under these conditions, the distance migrated by the solutes is usually expressed in relation to the distance migrated by the solvent, as has long been done for capillary analysis. This kind of information provides a measure of the adsorption capacity of columns; it reflects the adsorbability of the solutes, and it provides some information about the effect of one solute upon the adsorbability of another (*28, 29, 121*). With a given solute and solvent, this percolation method serves as a basis for the standardization of adsorbents (*73, 74*), and with a given solvent and adsorbent, it provides a means for the detection and identification of solutes. Because the analyst is concerned chiefly with the advancing boundaries of the migrating solutes, this continued percolation of solution through the adsorption columns is commonly called "frontal analysis" (*28, 128, 129*). This procedure never results in a complete separation of a single component from a mixture; hence frontal analysis is not equivalent to the complete chromatographic analysis as described by Tswett. It is more nearly equivalent to capillary analysis in its original form.

Adsorption of a small quantity of solution followed by development of the chromatogram remains the common procedure for the resolution of mixtures. Development of the chromatogram until the solutes are carried into the percolate is usually called the "flowing" or "liquid" chromatogram or "elution analysis" (*6, 28*). The amount and the concentration of the solution drawn into the column before development of the chromatogram influence the degree of separation of the bands and the distribution of the solutes in the bands (*121*). The smaller the amount of the solution the greater will be the separation of the bands, but the more difficult will be the detection of the bands, particularly those of the minor constituents. For example, in a small column, 0.03 microgram of chlorophyll b was required to form a perceptible band. Yet this amount of chlorophyll b could be detected in the presence of at least 2000 parts of chlorophyll a (*123*).

Development of the chromatogram with a series of solvents or solvent mixtures of increasing polarity, as first described by Tswett, often facilitates the separation of mixtures of similar substances (*118, 124*). When the solutes are carried into the percolate, this use of polar solvents is sometimes called "displacement development" (*28, 128, 129*). But variation of the solvent occasionally reverses the sequence or order in which the solutes separate in the columns (*118*); hence separations obtained by one solvent may be enhanced or they may be neutralized by the subsequent use of another (*118, 119*). When different mixtures of two solvents cause a binary mixture of solutes to separate in two sequences, there should be one mixture of the solvents that will not effect a separation of the solutes (*118*). Similar considerations should apply to mixtures of adsorbents. All these deductions point to obvious precautions that should be observed in the use of mixtures of solvents and mixtures of adsorbents.

There are many objectives in the use of chromatographic adsorption methods in addition to the resolution of mixtures and the isolation of the components. Some of these aims are the comparison of substances, especially those suspected of being identical, and the description and identification of substances by means of their adsorbability relative to that of various reference materials (*117, 118, 124, 150*). The reversal of the adsorbability with variation of the solvents may be utilized in order to remove the last traces of a less adsorbed substance from a more adsorbed substance (*82, 118, 124*). Additional examples of special objectives in the use of adsorption columns are presented in the sections devoted to adsorbents and to applications of the method.

Procedure and Objectives of Paper Chromatography. In the early applications of capillary analysis, one end of a strip of adsorptive paper was dipped into a solution and the distances penetrated by the solutes and by the solvent were compared. For the development of a paper chromatogram, a drop of the solution is commonly placed near one end of the paper strip, which is then dipped into the solvent (*77*). The paper may be held vertically as in the first applications of the capillary method (*143*) or it may be bent across a horizontal glass rod, so that gravity hastens the flow of the solvent and thereby aids in the development of the chromatogram (*35, 36, 116*). In long strips of paper, extensive development of a chromatogram may require nearly 24 hours, whereas comparable development in columns may require only an hour. Development of the chromatogram in paper must be performed in a closed vessel or cabinet in order to prevent excessive evaporation of solvent.

Chromatography in paper lends itself to the aptly called "two-dimensional development" or "cross capillary analysis" which was briefly described by Liesegang (*77*) and subsequently more extensively studied by Consden, Gordon, and Martin (*37*). In this method, a drop of the solution is placed near one corner of a square sheet of paper, an adjacent edge of which is then dipped into the developing solvent contained in a long narrow dish or trough (*78, 116, 145*). After the chromatogram has been formed, the paper is dried, and the edge adjacent to the chromatogram is dipped into another solvent, so that the chromatogram is developed farther in a direction at right angles to that of the first development. Under these conditions, the solutes appear as a series of spots distributed in a specific pattern in the paper (*35, 37, 77, 94, 95*). In columns, a comparable separation of solutes can be approached only by transference of the adsorbent from various sections of the chromatogram to a fresh column followed by further development with another solvent as has been done in the separation of chlorophylls from xanthophylls (*82, 124*).

In paper, extremely small quantities of complex mixtures may be completely resolved, especially by use of the two-dimensional chromatogram. A few micrograms of some 20 amino acids have been isolated and identified both in relation to their position in the paper and by the addition of reagents, such as ninhydrin, which form colored products with the separated acids (*36, 37, 44*). Similar results have been obtained by adsorption of sugars (*20, 44, 94, 95*) and other colorless substances. This use of reagents in paper is akin to the sensitive spot testing technique that has been widely employed by Feigl (*32, 33, 52, 53*). As in columns, radioactive substances in paper chromatograms can be located with photographic film or with counters (*44, 55, 115, 131*). Polarographic and enzymatic reactions may also be applied to solutes separated in paper (*67*). Dissolved salts and impurities in the solvents and in the paper often have pronounced effects upon the separability of mixtures of sugars and of amino acids (*94, 139*).

In general, the objectives of paper chromatography are identical with those of columnar chromatography. However, paper chromatography is not readily adaptable to use with very volatile solvents, with various adsorbents, or for large scale preparations (*97*). But the use of finely divided polysaccharides, such as cellulose pulp (*65*), cotton (*121*), starch (*90*), and cellulose acetate (*18*) in columns, overcomes some of these limitations of paper chromatography.

ADSORBENTS

Ion Exchangers. One of the major recent developments in the preparation and use of adsorbents has been in the field of ion-exchange compounds. A variety of organic ion exchangers of great combining capacity, of rapid exchange rate, and of highly reversible reaction are available commercially (American Cyanamid and Chemical Company, Dow Chemical Company, The Permutit Company, and Resinous Products and Chemical Company). Many of these ion exchangers, although formed in large particles or beads in order to facilitate rapid filtration, appear to be porous to the reactive ions and do not disintegrate upon repeated reaction and regeneration (*17, 58*). Particular properties of many of these products have been reviewed by Myers (*92*) and by Applezweig (*7*). Surface-active substances such as charcoal or alumina may be converted into ion-exchange adsorbents by preliminary adsorption of acids or bases (*70, 138*) just as cloth is rendered more attractive to dyes by treatment with mordants.

In columns, ion exchangers are especially useful for the separation of anions from cations, of ionic substances, as the alkaloids, from nonionic substances, and of mixtures of ionic substances that differ in valence. They also facilitate determination of the trace elements (*102*) and the total equivalence of acids and bases in salt solutions (*4, 79*). They have been used extensively in the separation of the rare earths and the products of atomic disintegration; some 113 pages of the *Journal of the American Chemical Society* have been devoted to a single symposium on this subject (*112, 113, 132*). In spite of all this effort, development of chromatograms in columns of ion exchangers has not reached a high state of perfection, although promising results have been obtained by the use of acids and of salt solutions as developers (*112, 113, 132*).

Partition Adsorbents. A solvent, as water or nitromethane, held in structural material, such as silica gel or diatomaceous earth, may sometimes serve as the adsorptive, stationary phase in an adsorption column (*2, 84*). In columns of these adsorbents, the solutes are, in effect, partitioned between two immiscible liquids, hence the term "partition chromatography" (*84, 86*). This use of partition adsorbents in columns is analogous to countercurrent extraction, particularly the fractional partition procedure improved so extensively by Craig (*21, 38, 39, 40, 88, 114*). Columns of partition adsorbents are useful for the resolution of mixtures of compounds which are decomposed by adsorption on surface-active substances, a noteworthy example being the separation of the penicillins (*13, 26, 56, 127*). But even under favorable conditions, amino acids were found to be bound by the silicic acid itself as well as by the water in the gel (*36, 84, 85*). With suitable solvents, partition adsorbents may have very great capacity for the adsorption of dissolved solutes.

When higher alcohols are used as solvents, water held by filter paper may also serve as the adsorptive phase, a phenomenon that has led to the term "paper partition chromatography" as indicated already (*36, 84*). With water as solvent, however, inorganic ionic substances may be held in paper by ion-exchange reactions as pointed out by Kolthoff some 30 years ago. Moreover, with water as solvent, the proteins phycocyanin and phycoerythrin are retained by the paper so that a mixture of these pigments can be separated as described by Kylin (*71*). Even with aqueous ethanol as solvent, the nonionic, weakly polar, fat-soluble chlorophylls and xanthophylls are bound by the surface-active forces of filter paper and can be separated from one another.

Surface-Active Adsorbents. Numerous investigations of the surface-active adsorbents confirm the enormous variability of their adsorption capacity and of their specificity or selectivity. Special attention has been given to the properties of diatomaceous earth (*5*), clays (*80*), magnesia (*152*), alumina (*91*), paper (*36*), starch (*90*), and many other substances (*43*).

The specificity of any given adsorbent, as indicated by the sequence in which substances are adsorbed in columns, may vary greatly with the solvent (*118, 120, 124*). This effect, which has been attributed, in part, to preferential affinity of the adsorbent for certain structural units or groups of the organic molecules (*119*), holds considerable promise for further investigation of the complex relationship between molecular structure and adsorbability.

Addition of fluorescent organic dyes or inorganic phosphors to nonfluorescent adsorbents facilitates the detection of colorless solutes that absorb ultraviolet light. In columns of these mixtures, the solutes appear as dark, nonfluorescent bands (*19, 108*).

Selection of Adsorbents. Mixtures of solutes may be resolved under such a great variety of conditions that the choice of adsorbents remains, to a great degree, a matter of trial and error. Indeed, by variation of the solvent and by adjustment of the concentration and the amount of the solutes adsorbed, mixtures of fatty acids and mixtures of amino acids have been resolved in columns of a variety of adsorbents such as the ion-exchange adsorbents, the surface-active adsorbents, and the partition adsorbents. In many uses of adsorbents, it is impossible to distinguish clearly among partition, ion-exchange, and surface-active forces, as all may be effective simultaneously. The number of variables is so great and experience is so limited that selection of adsorbents is determined to a greater extent by limited personal experience and by the objectives of the worker rather than by comparative results or by theoretical considerations.

In spite of all these complexities, the practical chromatographer has developed several procedures that serve as guides to the selection of adsorbents. When the nature of compounds in mixtures is known, selection of adsorbents can be based upon previous experience. With mixtures of unknown substances, a variety of adsorbents can be tested quickly in small columns. As a rule, the solutes should be weakly adsorbed so that they can be forced to migrate rapidly through the columns. In these exploratory experiments, the initial band of the adsorbed substances should not occupy more than about a tenth to a twentieth of the column, so that extensive development of the chromatograms will be possible (*119*). In these tests, the solvents should also be varied, because different solvents have a pronounced effect upon the adsorption capacity and the specificity of many adsorbents.

SOLVENTS AND ELUANTS

Selection of Solvents. The use of different kinds of solvents and eluants has scarcely kept pace with the increasing number of adsorbents. As the separability of mixtures varies tremendously with the solvent (*15, 37, 118, 119*), much more attention might profitably be given to the effect of solvents upon the relative adsorbability of various solutes.

In columns and in paper there must be an interaction between solvent and adsorbent and also an interaction between solvent and solutes in addition to the reaction between solutes and adsorbent. Disproportional variation of these forces may account for alteration of the adsorption sequence when solutions of chloroplast pigments in different solvents are adsorbed in columns of one adsorbent (*118, 119*). From this point of view, solvents may be selected so that they affect primarily the adsorbents or the solutes.

With surface-active adsorbents including filter paper, a variety of solvents ranging from water and the alcohols to the nonpolar hydrocarbons have been employed for the adsorption of various substances. Substituted cyclic nitrogen compounds and aliphatic and aromatic alcohols that are immiscible in water have found extensive use with the partition adsorbents (*37, 84, 90, 94, 95, 115, 116*). Solutions of acids and of organic ions have been utilized to adjust the equilibrium of inorganic ions between the ion-exchange adsorbents and the solvent so that the chromatograms are developed more effectively than with water alone (*112, 113, 132*).

Table I. Approximate Molecular Weights and Kinds of Substances Investigated by Chromatographic Adsorption Methods

Molecular Weight	Kinds of Substances
1–10	Hydrogen ion, smallest inorganic ions
10–100	Inorganic ions and smallest organic molecules such as alcohols, aldehydes, ketones, esters, and some amino acids
100–1,000	Heavy metal ions, complex inorganic ions, most synthetic organic compounds and many natural organic products such as sugars, fats, sterols, alkaloids, chlorophylls, carotenoids, amino acids, and antibiotics
1,000–10,000	Peptides, polysaccharides, phosphatides, etc.
10,000–100,000	Proteins including enzymes
100,000–1,000,000	Largest proteins and colloidal particles

Variable proportions of impurities in solvents often cause pronounced and unpredictable effects upon the adsorbability of various solutes. These effects, which may result in the alteration of the adsorption sequence of substances in a column (*118, 124*), complicate the standardization and interpretation of chromatographic adsorption procedures. On the other hand, when more fully understood, these effects of impurities may point the way to further refinement of the chromatographic adsorption techniques (*84, 90, 118*).

APPLICATIONS OF CHROMATOGRAPHIC ADSORPTION METHODS

One of the remarkable features of the chromatographic adsorptions methods is their wide applicability. All kinds of compounds of molecular weights from one to a million can be studied with adsorption columns provided these substances are soluble or dispersible in the liquids that are suitable for formation of the chromatograms. An indication of this wide applicability of the adsorption methods is provided by Table I.

There have been so many recent applications of the chromatographic adsorption method that it is impossible to present all of them, even in tabular form. As a consequence, selected applications that illustrate generalizations already presented in this review are summarized in Table II. In most of the examples, recent references have been cited so that they provide a key to the earlier literature.

PRINCIPLES OF CHROMATOGRAPHY

Mechanism. Chromatographic separations, either in paper or in columns, depend upon repeated partition of the solute between the adsorbent and the solvent. This repeated partition can take place only when there is a dynamic equilibrium among the solutes, the adsorbent, and the solvent.

A single solute molecule migrates in an adsorption column only while it is in solution. When it is held by the adsorbent, it remains stationary as the solvent flows past. The longer it is held by the adsorbent the slower it migrates. If two solute molecules differ in the time that they are retained by the adsorbent, they will migrate through an adsorption column at different rates. This dynamic effect may be illustrated by the mechanical model shown in Figure 1.

Rate of Migration of Solutes. Many molecules of a single solute migrate through an adsorption column at a rate which is determined by the flow of solvent and by the ratio of the molecules in solution to those adsorbed. On this basis, the distance moved by the bands of the adsorbed solutes is also related to the distance moved by the solvent.

$$\frac{\text{Amount solute not adsorbed}}{\text{Amount solute adsorbed}} = \frac{\text{distance moved by solute}}{\text{distance moved by solvent}} = R$$

(*28, 37, 73, 74, 84*)

This constant, R, has been determined in several ways. With partition adsorbents, R is determined in relation to the region of highest solute concentration in the middle of the symmetrical bands (*36, 84, 86, 90*). With surface-active adsorbents, R is determined in relation to the sharp leading boundaries of the unsymmetrical bands; hence R is sometimes represented by R_F (*37, 49, 73, 74, 84*). *An equivalent expression for the rate of* migration of ions in paper was formerly developed by Skraup and by Kolthoff, who recognized that R was a function of concentration, a complex relationship as shown by subsequent theoretical and experimental investigations (*24, 28, 29, 73, 74, 84, 93, 121, 137*).

The variation of R with concentration depends upon the properties of the adsorbents. With surface-active adsorbents, the amount of solute not adsorbed relative to that adsorbed increases with increasing concentration, as is well known from studies of adsorption isotherms (*24, 121, 137*); hence R increases with concentration. With partition adsorbents, R may remain relatively constant over wide variations of concentration just as the partition coefficient is known to be independent of concentration (*24, 37, 49, 84, 86*).

Determination of R at various concentrations of solute provides another method for estimation of adsorption isotherms (*73, 74, 113, 126, 132, 137*). This information provides a clue to the kinds of forces that are most effective in columns of a given adsorbent (*37, 49, 57, 73, 74, 113, 132*).

The rate of migration of one solute can also be described in relation to that of another. For the adsorption of sugars in paper this procedure is reported to yield reproducible values, but it introduces another variable (*20*). Identification of carotenoid pigments on the basis of their position above or below various reference materials (*118, 119, 120, 124*), involves, qualitatively, the same principles as those utilized in the estimation of the R value.

The amount of solvent which flows through an adsorption column before a solute appears in the percolate serves as a measure of the adsorption capacity of the column and is related to the R value. It is variously known as the "threshold volume" (*28, 73, 74, 92*), the "retention volume" (*28, 29, 128, 129*), and the "break-through volume" (*83, 92*), the last term being widely accepted in engineering practice (*83*).

Mathematical Interpretations. Following the basic work of Wilson and of DeVault, much progress has been made in the

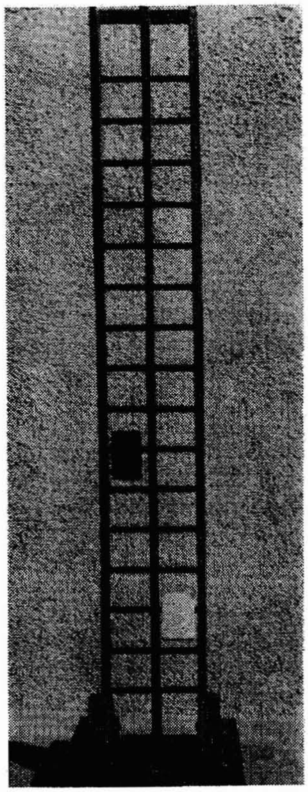

Figure 1. Mechanical Model Illustrating Separation of Two Different Molecules in Adsorption Column

The black "molecule" and the white "molecule" have different affinities for the adsorbent particles, the ladder rounds, and therefore descend the ladder column at different rates.

Table II. Substances Separated or Isolated by Adsorption and Adsorbents and Solvents Employed

Substances	Adsorbents	Solvents
Inorganic Substances		
Various rare earths		Aqueous solutions of citric and oxalic acids (*112*, *113*, *132*)
Fission products of uranium	Amberlite 1R-100	
Ions of salts	Paper	Phenol + water, collidine + water, etc. (*139*)
Inorganic ions	Zeo-Karb	Water and aqueous HCl (*58*)
Trace elements in salt solutions	Amberlite 1R-100	0.1 *N* salt solutions (*102*)
Various anions	Alumina	Water (*70*)
Fatty Acids		
Stearic and oleic acids	Charcoal + diatomaceous earth	Petroleum ether (*48*)
Higher fatty acids	Charcoal	Petroleum ether (*23*)
Tartaric and lower fatty acids	Amberlite 1R-4	Grape juice (*87*)
Lower fatty acids (*R* values)	Silica gel	Chloroform + butanol (*49*)
Various fatty acids		
In relation to molecular weight	Silica	Heptane (*31*)
In relation to chain length	Charcoal	Heptane (*31*)
Lower fatty acids as *p*-phenylphenyacyl esters	Dry silicic acid	Benzene + petroleum ether (*69*)
Nitrogenous lipides, amino acids, sugars	Paper	Phenol + water, collidine + water, etc. (*27*)
Fatty acids and bile acids	Foam	Water (*110*)
Phospholipides	MgO	Methanol (*125*)
Amino Acids		
Various amino acids (*R* values)	Paper	Collidine, benzyl alcohol, butyl alcohol, etc. (*37*, *143*)
Various amino acids (*R* values *vs.* concentration and spot size)	Paper	Phenol + ammonia (*57*)
Various amino acids	Ag_2S	Water (effect of pH) (*59*)
Various amino acids (retardation values)	Charcoal	Water + phenol (*128*, *129*)
Various amino acids	Charcoal, silica, Al_2O_3, etc.	Water, acids (*106*)
Acidic, neutral, and basic amino acids	Amberlite 1R-100	Water (*34*)
Basic amino acids	Wofatit C	Water, 1 *N* HCl (*141*)
Aspartic and glutamic acids	Amberlite 1R-4	0.01 *N* HCl (*47*)
Citrulline and allantoin	Amberlite 1R-100	Water at pH 6 to 7 (*8*)
Various amino acids		
From plants	Paper	Phenol + water, etc. (*115*, *116*)
From plants	Duolite resin	Water (*22*)
From liver	Paper	Phenol + water, etc. (*130*)
From silk hydrolyzate	Paper	Phenol + water, etc. (*97*)
From urine	Paper	Phenol + water, etc. (*44*)
Various amino acids as *p*-phenylazobenzoyl esters	$ZnCO_3$	Petroleum ether + 10% benzene (*68*)
Carbohydrates		
Various sugars (*R* values)	Paper	Phenol + water, collidine + water, etc (*20*, *95*)
Various sugars	Florex + Celite	Water, alcohols (*16*, *75*)
Sugars of milk	Amberlite IR-4B, Florex + Celite	Water, ethanol (*4*)
Uronic acid, sugars	Amberlite 1R-4B	Water (*20*)
Polysaccharide of *bacterium dysenteriae*	Paper	Phenol + NH_3 etc. (*94*)
Methylated sugars	Paper	Phenol + water collidine (*20*)
Various sugars	Cellulose pulp	Phenol + water etc. (*65*)
Antibiotics		
Streptomycin	Al_2O_3 charcoal	Methanol (*96*)
Penicillin G	Super Filtrol	0.05 *M* KH_2PO_4 (*127*)
Various penicillins	Paper	Amyl acetate (*146*)
Various penicillins	Silica gel	Ether or chloroform (*13*, *26*, *60*)
Various Isomeric Substances		
Benzene hexachlorides	Silica gel + nitromethane	Hexane (*2*)
d, *l* forms of Tröger's base	Lactose	Petroleum ether (*99*)
Brucine-*d*, *l*-mandelate	Glucose	Benzene (*61*)
l-Menthyl-*d*,*l*-mandelate	Alumina	Petroleum ether (*66*)
cis-trans-Carotenoids	Lime	Petroleum ether + various solvents (*15*, *149*, *150*)
cis-trans-Carotenoids	Sucrose	Petroleum ether + propanol (*124*, *122*)
Isomeric chlorophylls	Sucrose	Petroleum ether + propanol (*82*)
Enzymes		
Penicillinase	Hyflo Super-Cel	Water (*81*)
Flavine nucleotides	Paper	Collidine or butanol + acetic acid (*41*)
Glycerophosphatase	Al_2O_3	Water (*50*)
Various Carotenoids and Vitamin A		
Vitamin A, carotenes	Al_2O_3	Petroleum ether (*91*)
Vitamin A, carotenes, chlorophylls	Celite	Petroleum ether (*142*)
Vitamin A alcohol and ester	Al_2O_3	Ethylene dichloride (*100*)
Vitamin A_2	$AlSiO_3$, MgO, $ZnCO_3$	Petroleum ether (*109*)
Vitamin A aldehyde (retinene)	Al_2O_3	Petroleum ether (*9*)
Vitamin A aldehyde	$CaCO_3$	Petroleum ether (*136*)
Carotenes	Al_2O_3	Chloroform (*12*)
Carotene isomers	$Ca(OH)_2$	Petroleum ether + various solvents (*15*, *149*, *150*)
Carotenoids and chlorophylls	Sucrose	Petroleum ether + propanol (*119*, *120*, *124*)
Galloxanthin	$CaCO_3$	Petroleum ether + benzene (*135*)
Various Organic Substances		
3,5-Dinitrobenzoates of aliphatic alcohols	Silicic acid + filter aid	Hexane + ether (*140*)
2,4-Dinitrophenylhydrazones	Silicic acid + filter aid	Petroleum ether + ether (*104*)
Purines, pyrimidines, etc.	Paper	Butanol (*64*)
Anthocyanins (*R* values)	Paper	Butanol + acetic acid + water (*11*)
Hyoscine and hyoscyamine	Silicic acid	Benzene (*133*)
Coal bitumens	Silicic acid	Benzene, benzene + 5% ethanol (*72*)
Agent of chicken tumor	Celite	Aqueous NaCl (*103*)

mathematical description of chromatographic separations regarded as kinetic (*46*, *111*, *126*), partition (*38*, *39*, *40*, *84*, *86*, *88*, *114*), and adsorption (*28*, *46*, *93*, *126*, *137*) phenomena. The amount of solute adsorbed and the distribution of the solutes at the leading and trailing boundaries of the adsorption bands have been correlated with adsorption isotherms (*24*, *84*, *93*, *113*, *121*, *137*). Qualitatively there is excellent agreement between many deductions based upon the theories of adsorption and the phenomena observed in columns. Quantitatively, much additional precise information is needed in order to distinguish other important effects such as the rates of adsorption and desorption in columns (*113*, *126*, *132*), the effect of particle size, the effect of one solute upon the adsorbability of another (*29*, *128*, *129*), and the relationship between heat of adsorption and adsorbability (*91*).

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DISTILLATION

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THIS paper is written from the point of view of developments during the years 1946 to 1948. A few earlier papers are commented on or listed as references, but in general it is assumed that the earlier items of interest will be obtained by consulting the references in the more recent papers, or found in bibliographies or indexes.

Analytical distillation may be defined in various ways, but in this paper it is assumed to include simple laboratory distillation procedures and all the forms of distillation that involve rectification or fractionation regardless of whether quantitative analysis, qualitative separation, or mere detection is the objective. Production operations are naturally excluded, but preparative distillation, even on a pilot plant scale, is often of analytical interest.

Significant trends and developments in analytical distillation during the past several years have included the following:

Extensive utilization of fractionation in the analysis of complex mixtures of hydrocarbons, fluorocarbons, and many other types of compounds. Efficient fractionation has become a powerful and frequently used tool, so that success in achieving difficult separations or analyses is often a mere incident in solving broader problems.

Recognition of the limitations of distillation as a method of separation and analysis, and consequent combination of the process with various physical and chemical methods of analysis.

Realistic evaluation of analytical fractionation apparatus, with emphasis on time required, ease of operation, and actual separation at finite reflux in addition to the older use of theoretical plate standards at total reflux.

Improvement of older apparatus, particularly as to details and accessories, as well as the introduction of several entirely new types of contacting devices.

Development of special distillation apparatus such as rotary columns for vacuum distillation, small molecular stills, and apparatus for semimicro and microdistillation.

Further study and improvement of low temperature distillation, particularly by use of automatic controls to gain reproducible operation, and also by the use of simple isothermal distillation at low pressures to take advantage of the improved relative volatility, small sample size, and speed of analysis.

Limited progress in practical application of theoretical concepts, but considerable interest and activity along these lines.

Continued improvement and extension of A.S.T.M. distillation tests and similar methods involving simple standardized distillation as part of an analysis.

The relatively slow progress in catching up on the part of European scientists, except for general use of Podbielniak columns.

Publication of basic data and general bibliographies.

UTILIZATION OF FRACTIONATION

A classical example of successful analytical fractionation is the work of the National Bureau of Standards and its cooperating groups, dealing with the composition of petroleum (*45, 53–56, 119, 120, 138, 152*). This work is particularly notable for the balance between the use of distillation and other separation processes such as selective adsorption. Similar use of fractionation has been reported by the Bureau of Mines and others (*83, 126, 147*). Various complete fractionating columns have been developed or improved for general laboratory use (*40, 52, 61, 66, 69, 85, 90, 98, 113, 131, 136, 141, 143*). Extensive application of precise fractionation has also occurred in the development of fluorine chemistry (*11, 50, 104*). Almost all the papers in the 1947 A.C.S. Symposium on Fluorine Chemistry (*49*) describe or mention the use of distillation as a method of analysis or as a separation or purification step related to analysis. Other similar applications are widespread (*107*). The most recent involve the isolation of the oxygenated organics obtained from the Fischer-Tropsch or related processes. The prevalence of azeotropes in these mixtures complicates the use of distillation. There are no published papers as yet.

SPECIAL METHODS

Early enthusiasm for efficient fractionation led to the extreme of even attempting the separation of materials of almost identical volatility. This has been succeeded by a period of the development of a multitude of special tests which can identify components in the fractions resulting from the distillation. Such procedures are not new, but during the past few years there have been much more attention and activity in the perfecting of the special physical and chemical methods than in the associated distillation itself. Typical publications are cited (*30, 72, 78, 89, 119, 120*).

EVALUATION OF APPARATUS

Early evaluation of fractionating columns was confined almost entirely to the determination of the number of theoretical plates at total reflux. It has become increasingly evident that this is but one among many factors that determine the utility of a particular apparatus, and that it is easier to satisfy and measure plate requirements than some others. The American Petroleum Institute Symposium on High Temperature Analytical Distillation in November 1946 was a major contribution in the direction of overall evaluation. This series of papers dealt in detail with the results obtainable with heligrid, helices, perforated plate, and screen packings, and in columns ranging in size from those for samples of a few milliliters to gallon scale operation (*17, 21, 34, 40, 57, 66, 90, 114, 115, 152*). Among the factors considered were the time required to reach equilibrium, throughput rates, holdup, pressure drop, and deterioration, as well as theoretical plates at total reflux. Some attention has been given to determination of the latter at finite reflux (*34, 57, 117*) and to expression of results in terms of actual distillation curves instead of theoretical plates (*21, 57, 90*). Hilberath (*71*) has presented an interesting and thorough paper on column evaluation. Willingham and coworkers (*153*) have compared various columns and packings through use of the *A* factor. The evaluation of vacuum columns has progressed to the extent that several additional binary test mixtures have been developed (*47, 106, 151*).

IMPROVEMENT OF APPARATUS

A great variety of column heads and other devices has been presented for controlling and determining reflux ratio, for automatic fraction collection, and for automatic pressure control (*7, 8, 10, 24, 25, 39, 48, 63, 74, 79, 80, 87, 93, 121, 122, 142, 143, 149*). Lloyd and Hornbacher (*87*, 1947) listed 44 references to such devices. A critical summary and evaluation of these is much needed. Those for intermittent operation seem most practical, even though reflux and distillate streams may not always be divided in the exact proportions indicated by an automatic timer. There has been further discussion of the use of vacuum jackets compared with heated jackets to maintain adiabatic operation (*57, 66, 115*) and of the desirability of maintaining a forced temperature gradient (*108*). No clear-cut conclusions have been reached.

Most laboratory columns are heated by electric heaters, but with larger apparatus the time saving in bringing the charge to boiling with steam heaters is being recognized. Nearly uniform boilup rate is achieved by automatic controllers actuated by pressure drop between the still pot and the atmosphere (*21*). Improvements in relays have made it possible to simplify control circuits and to use water manometers to make and break the relay circuit. The use of a stream of nitrogen to prevent slow condensation of vapors from the still pot in the manometer lines is still common practice but will probably be succeeded by the simpler device of using a heated air reservoir. Langdon (*84*) has compared various still heating methods, and Schiff (*124*) has described a safety device for use with still heating jackets. A great variety of details regarding auxiliaries for fractionating columns is given in the papers of the American Petroleum Institute Symposium on High Temperature Analytical Distillation already cited, as well as in other descriptions of complete apparatus cited in connection with utilization or evaluation.

Mitchell and O'Gorman (*96*) have described a packing consisting of a wire helix of small diameter, wound in helical fashion around a central core to produce a device somewhat similar to the well known heligrid packing. Wire screen packing in the shape of Berl saddles has been developed and is known as McMahon packing (*88*). Dixon (*38*) has patented another type of screen packing. Protruded packings represent an entirely new type with unusual wetting characteristics (*29*). These will be valuable for the analytical columns of larger diameter.

DEVELOPMENT OF SPECIAL APPARATUS

The Bowman rotary vacuum still represents a completely new approach to the technique of fractionation (*28, 100*). The use of a cooled rotating central core to the column and heated outer walls gives a new type of operation (thermal rectification) of particular importance in vacuum fractionation. The distillation group at the National Bureau of Standards (*153*) has developed a more conventional rotary concentric tube column that operates by contact rectification, but has an unusually advantageous combination of height of equivalent theoretical plate (H.E.T.P.), holdup, pressure drop, and throughput characteristics. It too seems particularly adapted to vacuum operation. Birch, Gripp, and Nathan (*12*) have described a spinning band column for high vacuum and/or microfractionation, as have several other European authors (*13, 14, 76*). Donnell and Kennedy (*40*) described small concentric tube columns with take-off rates of 0.2 to 2 ml. per hour and a 6-mm. H.E.T.P. Several other micro and semimicrocolumns have been described (*32, 58, 59, 64, 91, 97*), as well as small molecular stills (*22, 37, 70, 105*).

Although there has been a large amount published on the industrial use of azeotropes, surprisingly little has appeared recently on their use in analytical distillation (*46, 154*).

Bowman and Sastry (*20*) have reported data extending Podbielniak's idea (*112*) that analytical percentages can be read directly from the temperatures along the length of a column that is operating at total reflux with the entire sample in the form of holdup.

LOW TEMPERATURE DISTILLATION

The Podbielniak low temperature apparatus (*68, 108–111*) has been steadily improved until it is a masterpiece of automatic and efficient separation of all except the closest boiling components such as the group of C_4 hydrocarbons boiling near 0° C. The use of various gaseous hydrocarbons in the manufacture of synthetic rubber and fuels has stimulated these developments. Procedures have been subject to an increased degree of standardization (*101*). The careful studies and comparisons of Savelli and co-workers are still of interest (*123*). The preparation of synthetic samples for purposes of evaluation and standardization of apparatus has been emphasized (*27*). Starr and co-workers have shown that relatively high charging rates may be used without loss in accuracy (*134*). The same group has also studied distillation rates and cut points (*133, 135*). Booth and McNabney have described an automatic column with anticipator control to decrease pressure surges (*16*). A few special accessories to low temperature apparatus have been described (*6, 26, 41, 42, 67, 144*). Shepherd (*129*) has reported the results of analysis of a standard sample of natural gas by laboratories cooperating with the American Society for Testing Materials. These demonstrated the need for standardization in procedures to obtain correct results. Shepherd and co-workers have also reported on sampling procedures (*130*) and on the National Bureau of Standards analytical procedures (*128*). Nelsen *et al.* (*102*) have presented nomographs for conversion of distillation temperatures and pressures of low boiling hydrocarbons to boiling points at 1 atmosphere.

Echols and Gelus (*44*) have given detailed descriptions of analyses of 2- to 50-ml. gas multicomponent samples by multiisothermal distillation. This involves simple vaporization and a series of observations on colligative properties such as vapor pressure, dew point, refractive index, and density. These data are used to calculate a curve of vapor pressure of the residual liquid versus per cent vaporization. The slope of this curve is related to the composition of any three-component system, and by determination of the slope at two points the composition of four-component systems may be fixed. By obtaining similar curves at selected temperatures, up to 14 components have been determined. Appleby, Avery, and Meerbott (*4*) have used multiisothermal distillation in studies of the thermal decomposition of *n*-heptane. Boomer *et al.* (*15*) have described an inverted apparatus for low temperature–low pressure fractionation.

APPLICATION OF THEORETICAL CONCEPTS

Better knowledge of the theory of batch fractional distillation could be of major assistance in analytical fractionation. This applies particularly to the choice of the quantity of charge and of the reflux ratio, and to estimates of the sharpness of separation to be expected. Various aspects of the theory have been presented (*18, 19, 33, 116*) but useful generalities are lacking. When holdup is appreciable, the effect of change of composition with time in batch distillation greatly complicates the relatively simple relations of steady state distillation. As a result, the use of a large charge may give a poorer separation than a small charge and separation may be as sharp at finite reflux as at total reflux. Westhaver (*153*) has made a further extension of basic theory in connection with the study of the rotary concentric tube column. Berg and James (*9*) and Coulson (*35*) have given information on the rate of approach to equilibrium in larger fractionating columns. Additional equations for estimating relative volatility from boiling point have appeared (*36, 94*).

SIMPLE DISTILLATION PROCEDURES

The applications of simple standardized distillation procedures and improvements are too numerous for specific mention. The 1947 A.S.T.M. Index (*3*) now contains 37 different procedures under the heading of distillation tests. These range from ammonia in phenol-formaldehyde molded materials to white linseed oil paints. A few other typical publications on specific analyses are cited (*2*, *5*, *31*, *43*, *51*, *60*, *65*, *75*, *86*, *92*, *127*, *140*, *148*, *150*). Many others no doubt exist, but are difficult to locate without special knowledge or the most detailed reading of the original literature. The bibliography of Rose and co-workers (*118*) contains a substance index which gives references to materials separated or determined by distillation, as obtained from papers or abstracts for the years 1941–45.

Codistillation was studied by Métayer in connection with the analysis of nicotine (*95*).

EUROPEAN ADVANCES

Journal articles of European origin vary a great deal in awareness of advances elsewhere. Some authors are up to date, but others lack an appreciation of the analytical possibilities of modern fractionating devices. A few only of the more comprehensive articles are cited (*1*, *62*, *81*, *82*, *103*, *125*, *137*).

BIBLIOGRAPHIES

The extensive vapor pressure tabulations of Stull (*139*) are of frequent application in approaching a new separation. Walas (*146*) has presented vapor pressure charts for organic materials. The compilations of properties presented by the National Bureau of Standards (*99*) and by Brown, Katz, and co-workers (*23*, *77*) are similarly useful. Horsley (*73*) has presented a condensed and systematic summary on azeotropes and nonazeotropes. Bibliographies of various degrees of selectivity and completeness have been published by Vilbrandt (*145*), Stage and Schultze (*132*), and Rose (*118*). The latter covers the years 1941–45 and includes abstracts of all papers on distillation as well as a subject and a substance index. The Stage and Schultze bibliography covers 1920–44 (though the war years are not complete) and has references with titles arranged according to subject matter. The Vilbrandt publication is highly selective with an engineering bias and covers the publication period of the principal American and English engineering and industrial journals to about 1946.

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EXTRACTION

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EXTRACTION has long been used analytically for preliminary separations of mixtures into groups. With present-day technique it can be further used to separate and quantitatively estimate the components of mixtures of closely related substances such as members of a homologous series. The basis for the first purpose is frequently that of solubility or of widely differing partition ratios. The basis for the latter is the use of a two-phase distribution in conjunction with a countercurrent process of some sort, so that separations may be made in spite of closely related partition ratios.

The approach for each of the two objectives may be similar or it may be entirely different, depending on whether or not partition ratios favorable for the purpose are possible. Thus, if a desired solute is present in a mixture and a solvent can be found which will extract only the desired solute, the simplest case is presented. If the particular solute is extracted exclusively but in part only, so that successive extractions are required, a more difficult case is to be treated and a countercurrent process may be desirable. In either case the only problem is that of performing the extraction so that the desired solute is completely removed from the accompanying substances. When such is the case in the literature considered, it is treated in the present review under the heading of "Extraction for Removal Purposes." On the other hand, when the problem is that of the separation of substances of similar solubilities or of similar partition ratios, a countercurrent extraction process is involved and the process is treated under "Extraction for Fractionation Purposes."

In order to limit the scope of the review, publications appearing before 1943 are not considered; otherwise, a short review would not be advisable. Even with this arbitrary restriction only those articles which appear to the writer to have a special interest are mentioned.

As regards previous review articles, the yearly reviews by Elgin (*21*) should in particular be consulted, although they are presented more from the standpoint of chemical engineering than from that of laboratory analysis. Green (*27*) has written a general review on extraction, but it too is written more from the preparative or commercial standpoint. An excellent review dealing mainly with the theory of such extraction has been written by Frey and Scheibel (*25*).

EXTRACTION FOR REMOVAL PURPOSES

Judging from the number of papers on the subject (*1, 32, 43, 46*), many chemists still have trouble with the continuous extraction of solids when amounts a little larger than ordinary laboratory quantities are encountered. Smaller amounts have apparently caused little difficulty. Wayman and Wright (*57*) have described efficient apparatus for the convenient extraction of small volumes of either light or heavy liquids.

Accounts have been published (*7, 24*) of the use of reduced pressures in order to perform extractions at lower temperatures and in inert atmospheres. A novel technique in analytical extraction, described by Harrison and Meincke (*29*), permits the use of pressure so that solvents which are gases at room temperatures may be employed. Often these solvents of low molecular weight have unusual or specific solvent properties. The apparatus is not elaborate. It involves the use of pop bottles with a synthetic rubber gasket for the cap and hypodermic syringes with a commercially obtainable stopcock fitted at the base of the needle.

Most research workers dealing with natural products sooner or later encounter difficulty with emulsions. Centrifugation is often time-consuming and ineffective. Emulsions usually result from surface-active solutes, but Davis (*19*) has published an interesting observation in this connection. When attempting to extract certain solutions which would otherwise cause trouble he found Duponol and Tween useful in preventing emulsions.

Pearl (*41*) and Kieselbach (*34*) have designed continuous extractors with settling chambers where the emulsions have time to break before being transferred to the concentration chamber. Extraction of fermentation liquors is often not easy. Two somewhat different continuous laboratory spray extractors (*12, 36*) have been designed to deal with this problem. In both the aqueous phase is injected into the organic solvent at one end of an unpacked column. Often stable emulsions do not form when the organic phase is present greatly in excess. In the Kolfenbach *et al.* extractor a single jet was used for injection of the aqueous phase. Air bubbles were continuously passed through the column to help break the emulsion. In the Bush and Goth extractor the aqueous phase was introduced through a distributor with many holes in it but the size of the holes was carefully controlled. Stable emulsions did not form when the holes were not smaller than a determined optimal size which, however, was small enough to give sufficient contact for good extraction.

In connection with the recovery of penicillin from fermentation liquors a number of interesting observations have been made (*44*) and a continuous countercurrent laboratory extractor has been designed for the purpose (*59*). Bush and Goth (*12*) designed their extractor for this purpose. The Podbielniak extractor (*42*), though too large for a laboratory analytical tool, is ideally suited for the commercial production of penicillin.

A common error in the use of an extraction procedure for analytical purposes is the belief that the distribution behavior of a pure substance can be used to predict its extractability from a crude mixture. In recent years a number of observations bearing on this point have been reported. For example, Dzialoszynski, Mystkowski, and Stewart (*20*) found that with certain organic solvents carotenes could not be extracted from aqueous solutions containing protein, though carotenes are not soluble in water but are fat-soluble. Extraction occurred readily at a lower pH. They postulated an association complex in order to explain the effect. Another example is the work of Heymann and Fieser (*30*).

Association of specific solutes is often recognized when the complex is less soluble than the separate components and therefore crystallizes out. Association can also be shown to occur in very dilute solution, by the solubilizing effect of certain solutes. The solubilizing effect of the higher fatty acids, certain proteins, certain sulfonic acids, the bile salts, saponins, etc., is well known.

Weil-Malherbe (*58*) has shown that this effect is also produced by the purines and has studied the influence on the effect of substitution on the ring structure. Unquestionably, the effect is in the same category as the phenomenon known as salting in but occurs at extreme dilution. In solution the complex may be largely dissociated, but the tendency to associate is present and may be considered in terms of an equilibrium constant. Often certain added substances in small concentration greatly reduce solubility (salting out). The reason may be that they associate preferentially with some component of the solvent which would otherwise associate with the solute, thus leaving the solute unassociated and less soluble.

Such effects may be extremely important in extraction. If the complex possesses a different partition ratio from the free solute it may defeat the purpose of the extraction. Conversely, it may form the basis of a highly useful analytical tool. Thus Brodie

(*10*) found that the dye methyl orange forms a salt or complex with antimalarial bases which partitions in a water-chloroform or serum-chloroform system greatly in favor of the chloroform. The free dye remains in the aqueous phase. Colorimetric determination of the dye in the chloroform gives a quantitative measure of the amount of base. With the use of other sulfonic acid dyes, the principle was earlier employed by Lehman and Aitken (*37*) for the estimation of Demerol and by Auerbach (*3*) for the estimation of certain quaternary bases. Titus and Fried (*54*) were able to partition streptomycin in a butanol-water system by addition of *p*-toluenesulfonic acid, whereas without the acid the antibiotic greatly favors the aqueous phase.

Obviously such effects offer an enormous field in extraction for future exploration. They also make somewhat more complicated the use of simple extraction as an analytical tool, particularly in biochemistry where substances with solubilizing activities are plentiful. When a complication from this source occurs, the use of systematic multiple extraction is often enlightening. Introduction of a known solid phase can be helpful (*23*) in extracting mixtures such as feces.

EXTRACTION FOR FRACTIONATION PURPOSES

Apparently certain advantages of the stepwise or discontinuous procedure over the continuous column procedures for analytical purposes have been fully realized only recently. In the discontinuous procedure (*5*) essential equilibrium can be reached at each stage and the factors required can be quantitatively studied in a very simple manner. In the continuous or column procedure, equilibrium between the phases is not reached and therefore the rate of exchange of the solute is important. The rate is known to depend on many factors, some purely mechanical. The efficiency of the column can therefore be derived only in terms of a height of column equivalent to a theoretical plate. Such a height often changes with the solute mixture, with the different solvents, and with slight changes in operating conditions. The relative partition ratios or separation factors also change with concentration unless dilute solutions are used. On the other hand, the discontinuous procedures can easily be made entirely reproducible. Concentrations at each stage can be calculated and held in a range of fairly constant partition ratios.

Bush and Densen (*11*) have studied systematic multiple extraction with individual units such as separatory funnels and have developed an ingenious systematization which they have called the diamond pattern. The system permits ready calculation of the fraction of a single pure substance which would be expected in each unit at the end of the process, provided the partition ratio remains constant. The importance of employing certain optimum volume ratios is discussed in their work.

Stene (*49*) has made an exhaustive mathematical investigation of systematic extraction procedures of many different types. He has shown the value in this field of the mathematics of probability and statistics. Craig (*15*), Williamson and Craig (*60*), and Lieberman (*38*) approached the problem on a similar but much more restricted basis. Craig (*15*) developed an apparatus by means of which multiple quantitative extractions could be done rapidly in a sequence, so that each step would correspond exactly to a term of the binomial expansion. The name "countercurrent distribution" was given to this particular type of extraction. It thus constitutes the simplest fractionation scheme possible. For exact mathematical interpretation a constant partition ratio is required. Apparently systems which give constant partition ratios are possible for the largest majority of substances, as the method has been applied with success to fatty acids (*2, 47*), aromatic acids (*31, 45*), phenols (*56*), penicillins (*6, 8, 9, 17*), antimalarial bases (*53*), streptomycins (*55*), xanthomycins (*50*), purines and pyrimidines (*51*), polypeptide antibiotics (*28*), and partial hydrolyzates of a protein or polypeptide material (*4, 61*). The method is sufficiently quantitative for wide application to the problem of purity (*14, 18*). Buffers of high salt concentration (*16, 47*) have proved useful. The analogy to the effect later obtained by Tiselius (*52*) in the use of salt solutions in chromatography is interesting.

A recent development of great analytical significance to biochemistry in particular is that called "partition chromatography" (*26*). The operation is performed as a chromatographic separation but the effect is considered by the originators, Martin and Synge (*39*), to be due to liquid-liquid extraction, since first an aqueous phase is adsorbed on some supporting agent such as silica, starch, or cellulose. The supporting agent forms a column and the immiscible organic phase is filtered through it. If the original view of the mechanics of operation is correct, then the process is similar to countercurrent distribution, except that it is a continuous process. This has now proved to be too simple an interpretation, as some of the better amino acid fractionations (*13, 40*) by the method have not required a second immiscible liquidphase. Furthermore, although certain band rates are in surprising agreement with that expected from a liquid-liquid partition ratio, many are in disagreement. It is also difficult to reconcile the degree of equilibrium apparently reached in the column with the difficulty expected for a purely liquid-liquid system (*5*) of this type. It would therefore appear that this development should best be reviewed under chromatography. An excellent review and bibliography on the subject of partition chromatography are given by Consden (*13*).

A certain amount of study has continued in the attempt to develop an efficient continuous liquid-liquid extraction column (*33, 35*), but the technical difficulties are considerable. In spite of the fact that separation factors with liquid-liquid extraction are usually much larger than with distillation and, therefore, such a column should be highly effective, a simple compact column which will furnish up to twenty stages was developed (*22*) only very recently. The column described by Scheibel (*48*) is of such design that it overcomes many of the mechanical difficulties in liquid-liquid extraction which contribute to the resistance of interchange of solute from one phase to the other and of clear-cut transfer or flow of the phases in the desired direction.

A promising approach where the required volatility is present is the more recent development known as "extractive distillation" (*22, 35*).

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ION EXCHANGE

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ALTHOUGH the recent availability of a host of ion exchange substances of various properties has stimulated the usage of ion exchange in analytical chemistry, the application of this phenomenon in analytical chemistry is not new. The use of Lloyd's reagent (*14*), a hydrated, aluminum silicate cation exchange substance, has found wide application for the removal of ammonia (*14*) prior to the determination of urea and for the analytical separations of amino acids (*3*). The concentration of solutions of trace elements on such cation exchangers as aluminum silicates (*1*) and filter paper (*10*) has been a common practice for many years. The consideration of ion exchange principles in the study of the nature of precipitates in gravimetric analysis (*21*), in elucidating the mechanism of the glass electrode (*11*), and in explaining glass electrode errors in dilute, unbuffered solutions (*12*) has been of considerable importance in analytical practices. The difficulties in storing extremely dilute solutions in glass bottles have also been attributed to ion exchange (*41*). However, these applications have been but a minor contribution to analytical chemistry in comparison with recent developments. The availability of ion exchange resins containing various functional groups and in several instances having an "analytical grade" purity has been responsible for many new contributions to the field of analytical chemistry.

The acceptance of ion exchange as an analytical operation or technique has not been universal, chiefly because the number of true analytical procedures involving ion exchange techniques have been few indeed. However, the possibility of utilizing ionic adsorbents such as ion exchange substances has opened many new vistas in analytical chemistry and it is probable that in the near future many new procedures founded upon ion exchange principles will be revealed.

The chief advantage of an ion exchange technique is that it enables one simply and rapidly to achieve a separation or concentration that would ordinarily be very difficult and time-consuming. In many applications of ion exchange in analytical chemistry, some accuracy and completeness of separation are sacrificed for simplicity and time. However, for many determinations, this sacrifice is well warranted.

The applications of ion exchange in analytical chemistry may be classified as (1) concentration of dilute solutions, (2) fractionation of ions having similar analytical properties, (3) removal of interfering ions, and (4) miscellaneous analytical applications.

A clear-cut distinction between some of the topics is lacking, because all the applications are based upon a common principle, the exchange of an ion in the ionic adsorbent with an ion in solution.

BASIC PRINCIPLES OF ION EXCHANGE

The phenomenon of ion exchange may take place, under certain conditions, in all ionic solids (and in some cases, insoluble liquids). If one considers the ionic solid to be completely dissociated—i.e., composed of ions and not undissociated molecules—the surface ions may then be considered as being bound to the lattice with a lower binding energy than the internal ions of the same species. When placed in a polar solvent, these surface ions may become solvated and a further lowering of their binding energy results and a marked dissociation from the lattice may also ensue. If a foreign electrolyte is added to the system, it is logical to expect an exchange to take place between these surface lattice ions and ions of the same charge of the foreign electrolyte. The extent of this exchange will depend upon (1) forces binding the ions to the lattice, (2) relative valences of the two ions entering into the exchange, (3) total concentration of ions, (4) sizes of the two ions, (5) accessibility of the lattice ions, and (6) solubility effects.

Commercial ion exchange substances (in particular, the ion exchange resins) are ionic solids in which one of the ionic species (either the anion or cation) is a highly cross-linked, polymeric, high molecular weight, nondiffusible ion whose multivalent charge is balanced by relatively small, diffusible ions of the

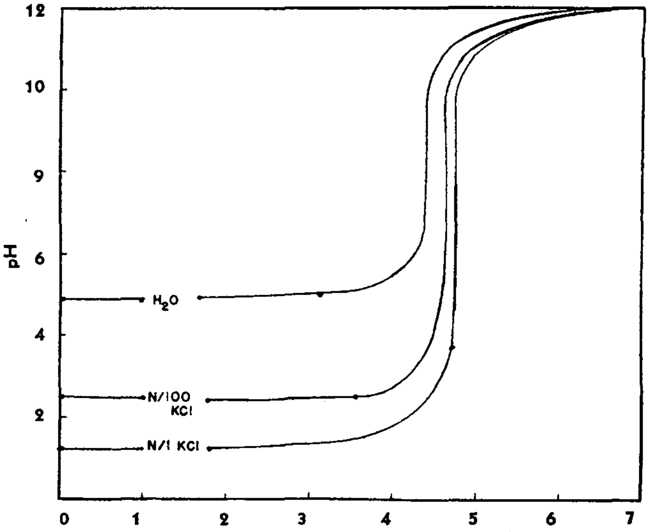

Figure 1. Titration of Amberlite IR-120 (*22*)
Nuclear sulfonic acid cation exchange resin

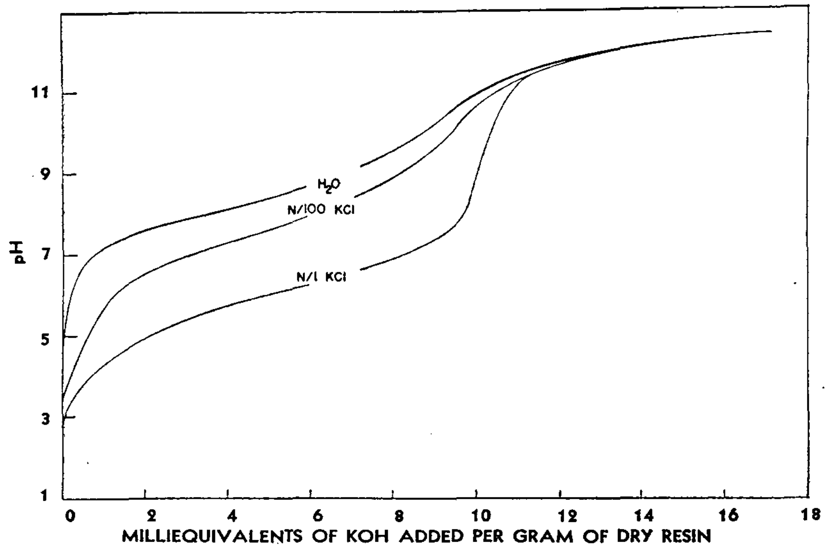

Figure 2. Titration of Amberlite IRC-50 (*22*)
Carboxylic acid cation exchange resin

opposite charge. These exchangers constitute a class of electrolytes having properties that are in many ways similar to true solutions of electrolytes. Ion exchangers having the properties of strong acids and bases, weak acids and bases, and intermediate acids and bases exist (*2*). The characteristics of these "ion exchange electrolytes" may be observed from the data in Table I and the equilibrium titration curves of Figures 1 to 5.

Many attempts have been made to establish a quantitative relationship for the various equilibria involved in ion exchange; however, although some success has been met for several ion pairs (*7, 28*), a vigorous and workable relationship has not been set forth. Qualitatively, one may approximate the extent of exchange for certain ion pairs, utilizing the following simple rules:

1. At low concentrations (aqueous) and ordinary temperatures, the extent of exchange increases with increasing valency of the exchanging ion ($Na^+ < Ca^{++} < Al^{+++} < Th^{++++}$) (*19*).
2. At low concentrations (aqueous), ordinary temperatures, and constant valence, the extent of exchange increases with increasing atomic number of the exchanging ion (Li < Na < K < Rb < Cs; Mg < Ca < Sr < Ba) (*19*).
3. At high concentrations, the differences in the exchange "potentials" of ions of different valence (Na^+ *vs.* Ca^{++}) diminish and in some cases *the ion of lower valence* has the higher exchange potential (*42, 53*).
4. At high temperatures (*18*), in nonaqueous media (*52*), or at high concentrations (*53*), the exchange potentials of the ions of similar valence do not increase with increasing atomic number but are very similar or even decrease.
5. The relative exchange potentials of various ions may be approximated from their activity coefficients—the higher the activity coefficient, the greater the exchange potential (*53*).
6. The exchange potentials of the hydrogen (oxonium ion) and hydroxyl ions vary considerably with the nature of the functional group and depend upon the strength of the acid or base formed between the functional group and either the hydroxyl or hydrogen ion—the stronger the acid or base, the lower the exchange potential (*22, 23*).

CONCENTRATIONS OF DILUTE SOLUTIONS

Ion exchange substances have been utilized as collectors for concentrating solutions containing an ion whose concentration is so low that the usual analytical procedures are inadequate for an accurate determination. The older procedures, such as coprecipitation and evaporation of large volumes, previously have been used with varying degrees of success but have been limited in their scope. The adsorption of the trace constituents on either a cation or anion exchange resin and the subsequent concentration by elution with a solution of higher concentration have shown considerable promise in the determination of traces of copper in milk (*11*) and of trace elements in plant matter (*32*). Lur'e (*26*) and Lur'e and Filippova (*27*) have recommended ion exchange for this purpose as a general procedure (*30, 46*). The data in Tables II and III indicate the accuracy that may be attained with this procedure. The advantages of the ion exchange concentration procedure are simplicity of operation, speed, and freedom of contamination. In order to achieve the foregoing advantages, a precaution must be exercised—i.e., the removal of all ionic impurities in the exchanger. It has been recommended (*11*) that the cation exchanger be thoroughly treated with hydrochloric acid and the anion exchanger thoroughly treated with alkali and each thoroughly rinsed prior to use.

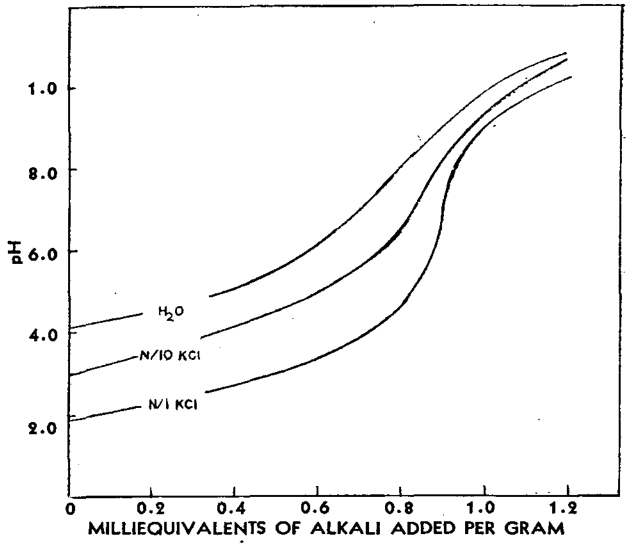

Figure 3. Titration of Electrodialyzed Bentonite (*53*)

Table I. Characteristics of Commercially Available Ion Exchange Materials

Name	Manufacturer	Type	Total Capacity Me./g.	Total Capacity Me./ml.
		Cation Exchangers		
Amberlite IR-100	Rohm and Haas	Phenolic methylene sulfonic	1.75	0.65
Amberlite IR-105	Rohm and Haas	Phenolic methylene sulfonic	2.70	1.00
Dowex 30	Dow Chemical	Phenolic methylene sulfonic	4.00	1.35
Duolite C-3	Chemical Process	Phenolic methylene sulfonic	3.25	1.00
Ionac C-200	American Cyanamid	Phenolic methylene sulfonic	2.70	0.81
Nalcite MX	Natl. Aluminate	Phenolic methylene sulfonic	3.00	1.15
Wofatit P	I. G. Farben	Phenolic methylene sulfonic	1.35	0.53
Wofatit K	I. G. Farben	Phenolic methylene sulfonic	2.50	1.00
Wofatit KS	I. G. Farben	Phenolic methylene sulfonic	2.45	0.90
Zeo Karb	Permutit	Sulfonated coal	1.62	0.60
Zeo Rex	Permutit	Phenolic methylene sulfonic	2.70	0.89
Amberlite IR-120	Rohm and Haas	Nuclear sulfonic	4.20	2.15
Dowex 50	Dow Chemical	Nuclear sulfonic	4.25	2.20
Nalcite HCR	Natl. Aluminate	Nuclear sulfonic	4.15	2.10
Alkalex	Research Products	Carboxylic	4.95	1.80
Amberlite IR C-50	Rohm and Haas	Carboxylic	10.0	4.20
Duolite CS-100	Chemical Process	Carboxylic	3.85	1.11
Permutit 216	Permutit	Carboxylic	5.30	1.70
Wofatit C	I. G. Farben	Carboxylic	7.00	2.50
Montmorillonite	......	Aluminum silicate	0.8–1.2	...
Kaolinite	......	Aluminum silicate	0.06–0.10	...
Glauconite	......	Aluminum silicate	0.18–0.2	...
Permutit	Permutit	Aluminum silicate	1.0–3.0	...
Decalso	Permutit	Aluminum silicate	...	...
Zeo Dur	Permutit	Aluminum silicate	...	...
Silica gel	......	Silicic acid	0.01–0.04	...
		Anion Exchangers		
Amberlite IR4B	Rohm and Haas	Weak base	10.0	2.50
Amberlite IR A-400	Rohm and Haas	Strong base	2.3	1.00
De Acidite	Permutit	Weak base	9.3	1.5
Duolite A-2	Chemical Process	Weak base	7.0	1.20
Duolite A-3	Chemical Process	Weak base	6.8	1.10
Ionac A-300	American Cyanamid	Intermediate base	7.4	1.50
Wofatit M	I. G. Farben	Weak base	...	1.20
Alumina	......	Amphoteric	0.01	...

Table II. Comparison of Ion Exchange Methods for Determining Silica with Other Procedures

(Data of Cranston and Thompson, *11*)

Sample	Spectrophotometric P.p.m.	Polarographic P.p.m.	Ion Exchange P.p.m.
Raw fluid milk	0.15	...	0.15
Powdered whole milk	0.15	...	...
Powdered whole milk	15.2	...	15.0
Ice cream mix	0.65	...	0.45
Nonfat milk solids	...	1.1	1.1

The degree of concentration that may be attained by means of ion exchange depends largely upon the capacity of the exchanger and type and concentration of elution agent that may be tolerated in the final determination of the ionic constituent or constituents in question.

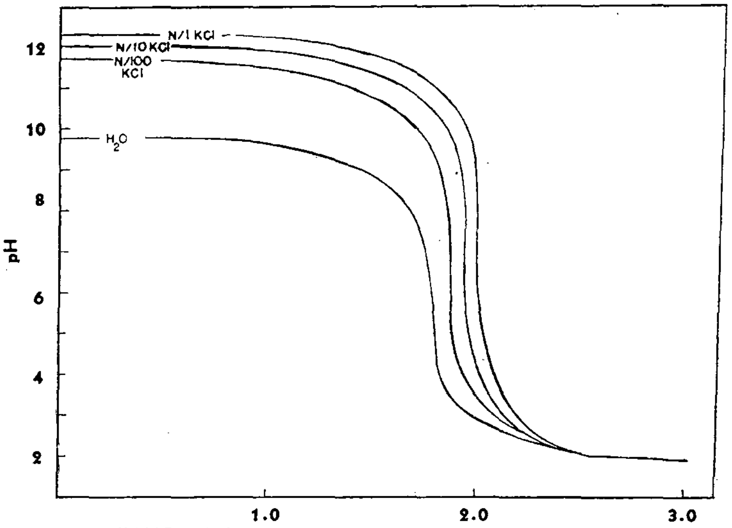

Figure 4. Titration of Amberlite IRA-400 (*23*)

Strong base anion exchange resin

The concentration of solutions by ion exchange represents an improvement of previous adsorption and coprecipitation procedures and will undoubtedly prove useful in the analyses of trace elements.

FRACTIONATION OF IONS HAVING SIMILAR ANALYTICAL PROPERTIES

Although there are many cases in analytical chemistry in which the analysis of a particular ionic constituent is most difficult because of the presence of other ions having closely related properties, the rare earths and the amino acids are two outstanding cases, one in inorganic and one in organic analysis. The application of chromatographic techniques using ion exchange substances as adsorbents has aided considerably in the analysis of both rare earths and amino acid mixtures. The principles involved in this technique are similar to those involved in the chromatographic analysis of nonionic constituents; however, superimposed on these principles are several added ones involving ion exchange. In brief, the mixture of the difficultly separable ions is adsorbed at the upper end of an exchange column. The "chromatogram" is developed by displacing these adsorbed ions with a foreign ion of like charge. Because of a difference (which may be slight in many cases) in exchange potential, the two ions tend to separate into bands as the foreign ion replaces them. The sharpness of separation depends upon several factors, such as (1) differences in exchange potential, (2) nature of elution agent, (3) length of column, (4) degree of column loading, (5) flow rate during development of band, and (6) particle size.

Table III. Recovery of Metallic Traces by Ion Exchange

(Data of Riches, *32*)

Elements	Cu	Cd	Ni	Zn	Mn
	γ	γ	γ	γ	γ
Quantity introduced	20	40	20	20	20
Total recovered	18.8	38.4	19.7	19.0	17.4
% recovered	94	96	99	95	87

The separation of the rare earths by ion exchange illustrates the effect of the above variables remarkably. The similarity of various rare earths necessitates the use of a complexing agent in order to further the separation factor. The use of carboxylic acids such as citric, tartaric, etc., as eluting agents markedly enhances the separation. The action of the complexing agent depends upon the differences in ionic equilibria between the various rare earths and the carboxylic acid. Several investigators (*7*, *20*) have found that the differences in ionic equilibria of these complexes are very dependent upon pH and that the optimum pH may vary with the concentration of the complexing agent. Figures 6 to 11 describe the effects of these and other variables clearly.

Similar chromatographic techniques have been applied to the fractionation of amino acids by ion exchange methods. Several investigators (*8*, *48*) have shown that glutamic and aspartic acids

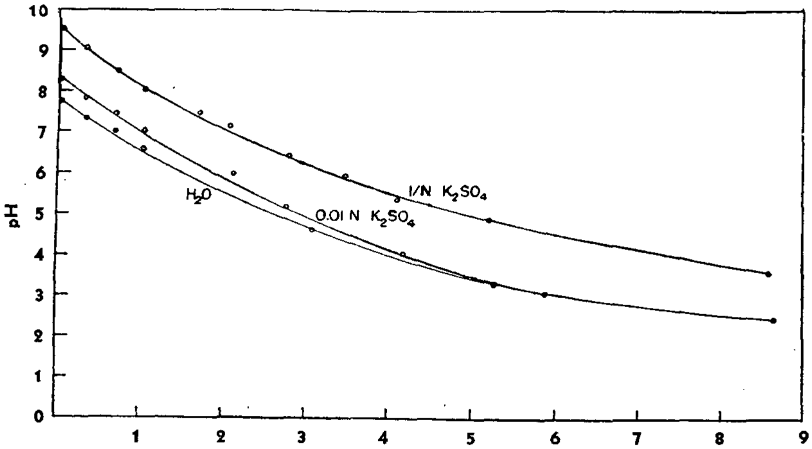

Figure 5. Adsorption of Sulfuric Acid in Potassium Sulfate Solutions by Amberlite IR4B (*24*)

Weak base anion exchange resin

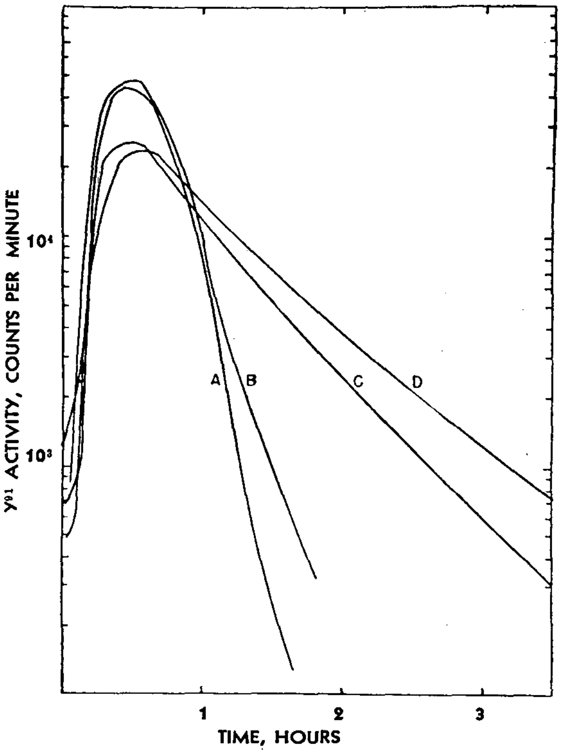

Figure 6. Effect of Mesh Size of Amberlite IR-1 on Desorption Band Width (*20*, p. 2806)

A. **270- to 325-mesh**
B. **170- to 200-mesh**
C. **50- to 60-mesh**
D. **30- to 40-mesh**

may readily be separated by the application of these chromatographic techniques using an anion exchange column as the adsorbent. Drake (*13*) has designed a recording microapparatus for the separation and estimation of these amino acids. As the amino acids are amphoteric and exhibit isoelectric pH's that vary over a considerable range, it has been possible to achieve group separations based upon the use of a series of exchangers having functional groups that will be active only towards amino acids having an isoelectric pH within certain limits. By adjusting the pH, it is possible to change the ionic composition of the amino acid mixture so that only a selected group will be capable of being adsorbed by a specific exchanger. Cannan (*8*), Tiselius, Drake, and Hagdahl (*48*), and Winters and Kunin (*54*) have devised procedures for the separation of the amino acids into the three basic charge groups—acidic, neutral, and basic. The latter procedures are outlined in Figure 12.

Although ion exchange substances may be utilized for the chromatographic separation of any ionic mixture, many techniques may be employed with ion exchangers for achieving ionic separations without resorting to chromatographic principles. If a considerable difference exists in ionic size, basicity, acidity, or valence, it is possible to achieve these separations. Myers, Eastes, and Urquhart (*31*) have demonstrated that it is possible to separate completely chlorides and sulfates directly upon passage of the corresponding acids through an anion exchange resin. During the passage through the column, sulfate ions, being divalent, are adsorbed preferentially at the top of the column. A glance at the data in Table IV indicates the clear-cut separation of chlorides and sulfates that may be achieved.

Similarly, one may separate small quantities of the divalent calcium from monovalent sodium ions. The passage of a solution hundredth normal with respect to both sodium and calcium ions through a column of the sodium form of a cation exchange resin will result in a complete adsorption of calcium ions and at the break-through point the resin will practically be void of sodium ions and nearly saturated with calcium (*29*).

Separations based upon differences in basicity and acidity may be achieved with various exchangers by choosing the appropriate exchanger that has either the acidity or basicity that

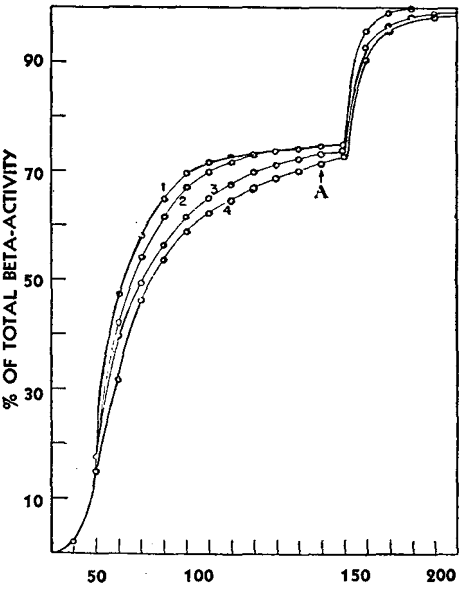

Figure 7. Separation of Divalent and Trivalent Fission-Produced Radioisotopes by Complex Elution from Amberlite Resin and Effect of Rate (*49*)

Resin. **Amberlite IR-1, 40- to 60-mesh, hydrogen form**
Bed. 0.75 sq. cm. × 13 cm.
Influent. **5% citric acid plus ammonia to pH 3.00 (up to *A*), to pH 6.00 (after *A*)**
Flow rate. **1, 2, 5, and 10 ml. per min. in curves 1, 2, 3, and 4, respectively**
Source of tracers. Mixed fission products obtained in carrier-free state by extraction of uranium from dissolved, pile-exposed uranium
Analyses indicate near-quantitative removal of Y, Ce, rare earths, Zr, and Cb only up to *A*, similar removal of Sr and Ba after *A*

is sufficiently strong to neutralize but one ionic component or species of a mixture of electrolytes. The weak acids such as hydrocyanic, hydrogen sulfide, phenol, and carbonic and silicic acids, may readily be separated from the stronger acids, hydrochloric, sulfuric, phosphoric, etc., on passage through a bed of a weakly basic anion exchange resin, an exchanger not sufficiently basic to neutralize the weak acids (*23*). Similarly, one may achieve separation of bases by choosing the appropriate cation exchanger. For example, a carboxylic exchanger may be utilized for the separation of the more weakly basic alkaloids (strychnine, caffeine) from the more basic ones such as quinine, brucine, and nicotine (*54*).

Separations based upon ionic size differences are striking when one of the ions is of such size that it cannot diffuse into the interior of the exchanger. The choice of an exchanger whose structure is such that only the exchange of the smaller ionic species is feasible will enable one to achieve the separation of certain macro ions from normal sized ions. Cernescu (*9*) has shown that the natural zeolite, chabazite, will adsorb ammonium ions but that only negligible amounts of the tetramethylammonium ions may be adsorbed (see Table V). The decrease in the exchange capacity of sulfonic and carboxylic exchanger for large ions may be observed in Figure 13. These data indicate that these exchangers may readily be used for the separation of the relatively small inorganic ions from the complex organic ions (*25*). As the large ions may be adsorbed and exchanged with ions at the exchanger surface, it is obvious that the particle size of the exchanger that is to be used must be large enough so that the surface contribution is but negligible. Particles of 0.5 mm. are satisfactory.

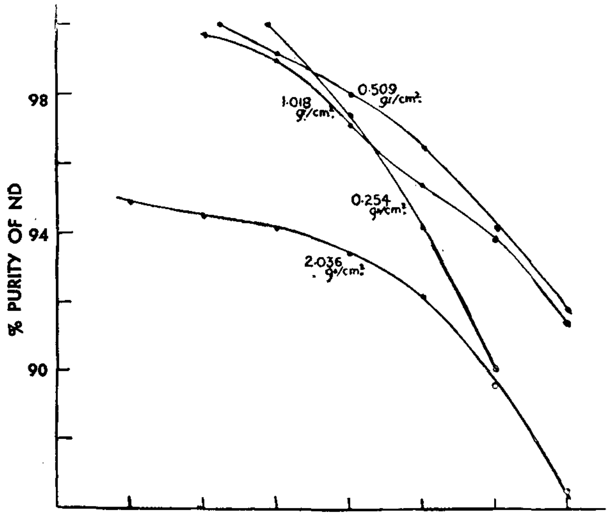

Figure 8. Change in Separations with Change in Weight of Sample Using Longer Columns (*45*, p. 2788)

Column dimensions. 16 mm. × 350 cm.
Flow rate. 6 cm. per min.
pH. 2.66
Composition of starting material. 56.6% Nd with 43.4% Pr

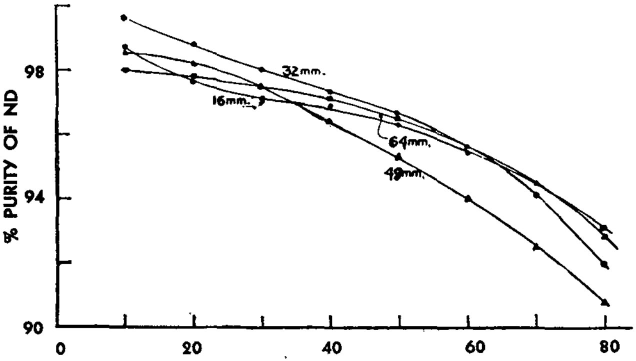

Figure 9. Effect of Column Diameter on Separation (*45*, p. 2789)

Column length. 175 cm.
Composition of starting material. 80% Nd with 20% Pr
Weight of sample. 0.50 gram per sq. cm.
Flow rate. 6 cm. per min.

Table IV. Separation of Chloride and Sulfate Ions with an Anion Exchange Resin

(Data of Myers, Eastes, and Urquhart, *31*)

Section of Column	% S	% Cl	Color
1 (top)	11.64	0.00	Orange
2	11.59	0.00	Orange
3	11.59	0.00	Orange
4	11.36	0.00	Orange
5	...	1.17	Orange
6	3.20	12.32	...
7	0.00	18.31	Brown
8 (bottom)	0.00	13.00	Brown

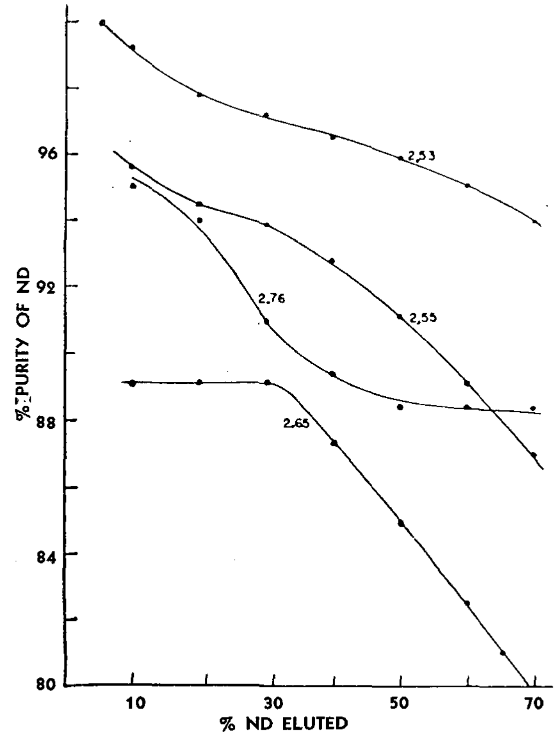

Figure 10. Effect of pH on Separation (*45*, p. 2787)

Column dimensions. 16 mm. × 175 cm.
Flow rate. 5 to 6 cm. per min.
Composition of starting material. 79% Nd, 21% Pr for 2.53 and 2.76 experiments and 57% Nd, 43% Pr for 2.55 and 2.65 experiments

REMOVAL OF INTERFERING IONS

In many analytical procedures, one may encounter extreme difficulties due to the presence of a foreign ion. The foreign ion

Table V. Relation between Structure of Silicate Exchanger and Exchange Capacity toward Ions of Varying Radii (*9*)

Ion	Ionic Diameter, *R*	% Total Capacity Realized (10% Error)	
		Clay	Chabazite
NH_4^+	2.90	100	100
$CH_3NH_3^+$	3.18	95	21
$(CH_3)_2NH_2^+$	5.94	88	9
$(CH_3)_3NH^+$	6.54	98	9
$(CH_3)_4N^+$	6.98	106	4

need not have similar analytical properties but may interfere because of complex formation, coprecipitation, *etc.* In certain cases, the interfering ion may be of the opposite charge—for example, phosphates interfere in the analysis of sodium by the zinc–uranyl acetate method and in the analysis of calcium and barium by the oxalate and sulfate procedures. In many cases considerable difficulty has been avoided by the simple and rapid removal of the interfering ions with ion exchange substances.

The technique of using ion exchange substances for the removal of interfering ions has found wide application, especially for those cases in which the charge of the interfering ion is the opposite of the charge carried by the ion to be determined. Although many instances have been reported in the literature, only a selected few are discussed here, since they fully describe the principle involved.

Samuelson (*33–40*) has fully investigated the separation of many cations from anions that may possibly interfere in the estimation of either the anion or the cation. Quantitative separations have been found for the following systems:

Halides of Na^+, K^+, NH_4^+, Mg^{++}, Ca^{++}, Si^{++}, Ba^{++}, Co^{++}
Sulfates of Na^+, K^+, NH_4^+, Mg^{++}, Ca^{++}, Zn^{++}, Mn^{++}, Co^{++}, Al^{+++}, Fe^{+++}

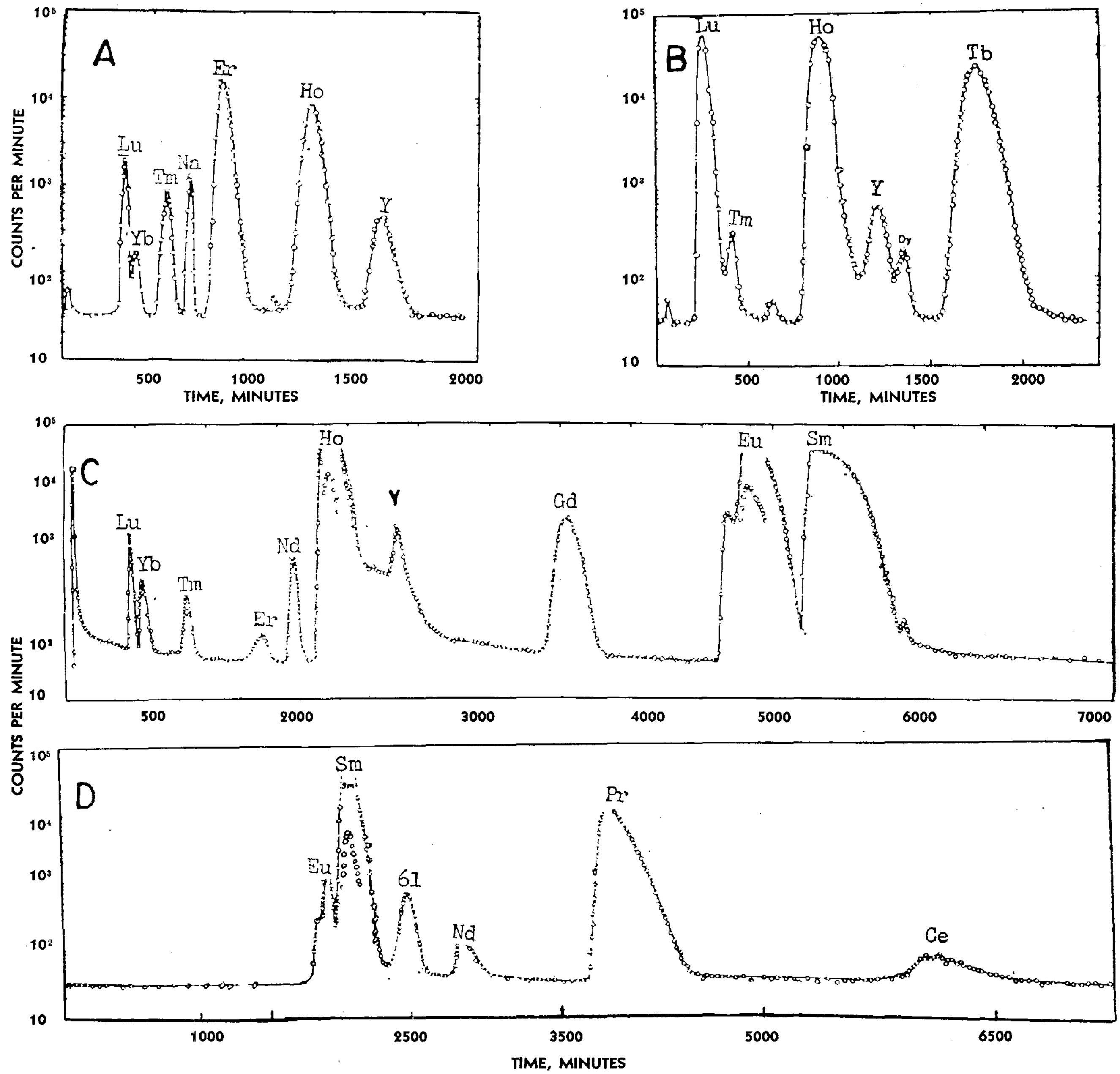

Figure 11. Demonstrations of Rare Earth Separations (*20*, p. 2808) Effected with 270- to 325-mesh Dowex-50 column at 100° C.

Bed dimensions. 97 cm. × 0.26 sq. cm.
Flow rate. 1.0 ml. per sq. cm. per min. except in *A* where 2.0 ml. per sq. cm. per min. was used
A. Fractionation of activities produced by neutron irradiation, 0.8 mg. spectrographed grade Er_2O_3 (Hilger). pH 3.20
B. Fractionation of heavy rare earth mixture consisting of 0.1 mg. each of Lu_2O_3, Yb_2O_3, Ho_2O_3, and Tb_2O_3 Tm, (Er), Y, and Dy present as impurities. pH 3.20
C. Fractionation of intermediate rare earth mixture consisting of 0.1 mg. Ho_2O_3 and 1.0 mg. each of Dy_2O_3, Gd_2O_3, Eu_2O_3, and Sm_2O_3. Cl, Lu, Yb, Tm, Er, and Na present as impurities. pH 3.25 for 4550 minutes, then pH 3.33
D. Fractionation of light rare earth mixture consisting of 0.1 mg. each of Sm_2O_3 and Nd_2O_3 plus 0.01 mg. each of Pr_2O , Ce_2O_3, and La_2O_3, Eu present as impurity, 61 produced by 1.7 h Nd^{149} 47 h 61^{149}. pH 3.33 for 1610 minutes then pH 3.40

Nitrates of Na^+, NH_4^+
Perchlorates of Ni^{++}, Co^{++}
Acetates of K^+, Na^+, NH_4^+, Ca^{++}, Ba^{++}, Mg^{++}, Sr^{++}, Pb^{++}
Phosphates of Si^{++}, Ca^{++}, Ba^{++}, Mn^{++}, Zn^{++}, Co^{++}, Ni^{++}, K^+, Na^+

These systems may be separated with the hydrogen form of the sulfonic acid cation exchange. For systems in which the corresponding acid of the salt is either unstable or insoluble, the ammonium form of the exchanger has been recommended. Samuelson has found quantitative separations for the sodium and potassium salts of the complex cyanides of iron, chronium, cobalt, molybdenum, and tungsten, and for the simple chromates, molybdates, tungstates, phosphomolybdates, silicotungstates, and metavanadates. It appears that quantitative separations may be made of all systems except for such salts as chromium sulfate in which the chromium may exist in part as a neutral or even an anionic species.

Samuelson (*34*) has shown that in the determination of the alkali metals in the presence of phosphate, the interference of phosphate may readily be eliminated by passing the solution through a sulfonic acid exchanger, rinsing, and eluting with an ammonium chloride solution. The ammonium chloride is then removed by evaporation and mild ignition. This procedure is more rapid and less subject to error than the use of a phosphate precipitation. Similar procedures have been recommended by Samuelson for other interfering anions. In a similar manner one may avoid the difficulties in the determination of calcium as calcium oxalate in the presence of phosphates.

In the gravimetric determination of sulfate as barium sulfate, errors are encountered because of the coprecipitation of foreign cations such as sodium, aluminum, and iron. Sodium is troublesome when the sulfate is to be determined in the solution resulting from a Parr bomb fusion. The removal of these interfering elements can be readily accomplished by the passage of the solution through the hydrogen form of the sulfonic acid cation exchanger.

The determination of phosphorus pentoxide in apatite has been shortened considerably by Helrich and Rieman (*17*), utilizing a technique similar to the one already described. The apatite is digested in hydrochloric acid and evaporated to dryness to stabilize the silica and to remove the fluorides. The residue is redissolved and filtered, and the resulting solution is passed through a column of the hydrogen form of a sulfonic acid exchanger. This step converts the phosphates and chlorides into hydrochloric and phosphoric acids. The phosphorus pentoxide is determined by titration with standard alkali. The titer between the methyl orange and phenolphthalein end points is equivalent to the phosphorus pentoxide.

The analysis of many substances may readily be simplified when the constituent to be determined is the only anion or cation (except for trace amounts of other substances) present. If this assumption can be made without any appreciable introduction of error, an ion exchange substance can be used to facilitate the rapid analysis of many substances. For example, in the analysis of commercial samples of alum, ammonium nitrate, calcium sulfite, and sodium sulfite, Samuelson (*33*) has shown that the sulfate in alum, the ammonia in ammonium nitrate, and the calcium and sodium in the sulfites can be determined accurately by conversion of the salts to the corresponding acids by ion exchange and titrating the resulting acid. This procedure is most helpful for standardizing solutions that are prepared

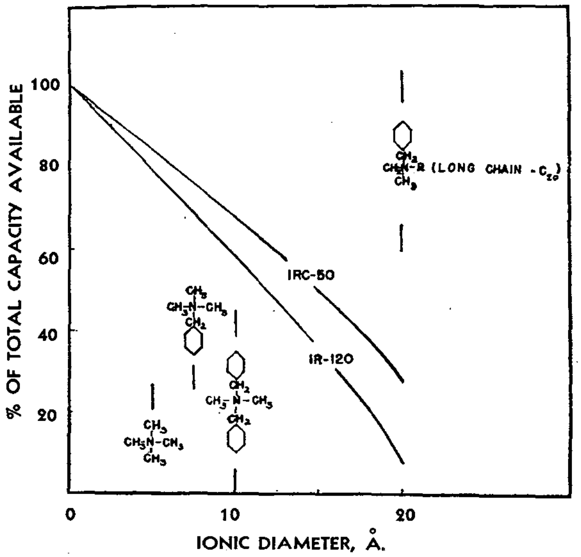

Figure 13. Effect of Ionic Diameter on Total Available Exchange Capacity

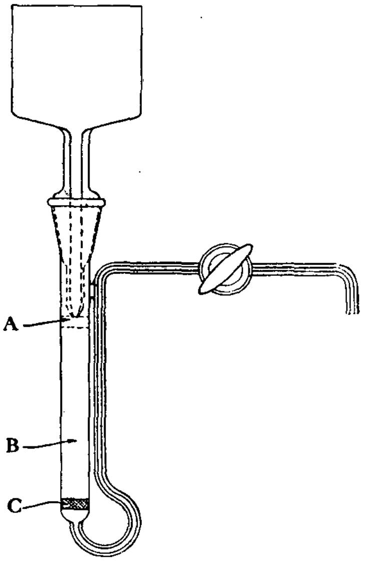

Figure 14. Experimental Column (*49*)

Funnel is removable to facilitate resin addition and removal. Resin bed, *B*, is 1 sq. cm. × 10 cm. and rests on porous glass disk, *C*. Stopcock in outlet tube allows regulation of flow rate. Opening in outlet tube is above top of resin bed, thus maintaining liquid layer, *A*, above resin at all times

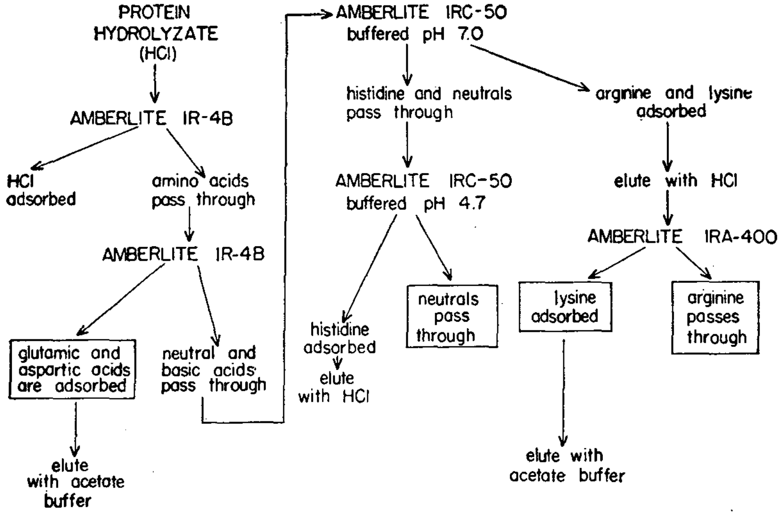

Figure 12. Scheme for Separating Amino Acids with Ion Exchange Resins (*54*)

from pure salts that cannot be dried to a definite weight with reasonable accuracy.

Lur'e and Filippova (27) suggest the use of cation exchangers for the separation of amphoteric substances (molybdenum, tungsten, zinc, aluminum) from nonamphoteric substances (iron, copper) employing the exchanger as an adsorbent for these ions and then eluting with sodium hydroxide in order to precipitate the latter group. However, this procedure has no advantage over a precipitation procedure without exchangers except for those cases in which dilute solutions are involved. In these cases, the exchanger serves as a collector and means for concentration.

MISCELLANEOUS ANALYTICAL APPLICATIONS OF ION EXCHANGE

Determination of Total Electrolyte Concentration. In many laboratories, the analyst is interested in determining the total electrolyte concentration of a solution or extract containing a mixture of several electrolytes. Although the conductance of such a solution may yield a satisfactory value, owing to the complexity of the solution, in some cases, the conductivity data cannot be accurately interpreted in terms of a concentration unit. The analyses of water supplies (4), soil extracts, plant extracts, serums, etc., are examples of the foregoing solutions.

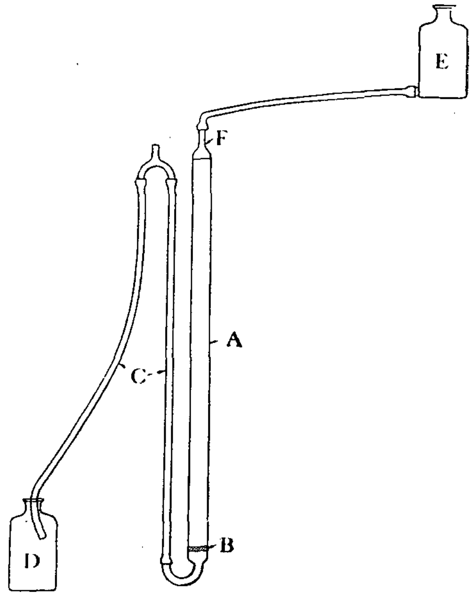

Figure 15. Typical Column Apparatus (16)

Resin bed, *A*, rests on porous disk *B*, in glass column *F*. Flow rate is adjusted by varying height of bottle *E*, which contains influent solution. Effluent is collected in bottle *D*. Vent in tube *C* ensures continuous liquid layer over resin bed

Again, one may utilize the hydrogen form of a sulfonic acid cation exchanger. The solution is merely passed through a column of the exchanger and the resulting solution titrated with standard alkali. However, in certain cases, the original solution may contain hydroxides, carbonates, or bicarbonates and for these electrolytes the hydrogen exchange does not release an equivalent amount of acid. It then becomes necessary to titrate the original solution for any alkalinity before passage through the column. Studies of this method have been reported by Samuelson (33) and Myers (29).

Determination of Mean Atomic Weights. In the analysis of rare earth mixtures, the mean atomic weight of the mixture has been used as a criterion of its nature. Although several procedures have been used, a typical method involves the precipitation of the oxalates of duplicate aliquots. One of the precipitates is titrated with permanganate and the other ignited to the oxide. By means of these values, it is then possible to calculate the weight of the rare earth mixture that is combined with a given weight of oxalate, from which may be calculated the mean atomic weight of the rare earth mixture. This procedure may be simplified by passing a solution of the rare earth mixture through the hydrogen form of the sulfonic acid cation exchanger and titrating the liberated acid. The resin may then be ignited, leaving the residue of the rare earth oxides. The mean atomic weight may be calculated from the titer and oxide weight as with the previous procedure.

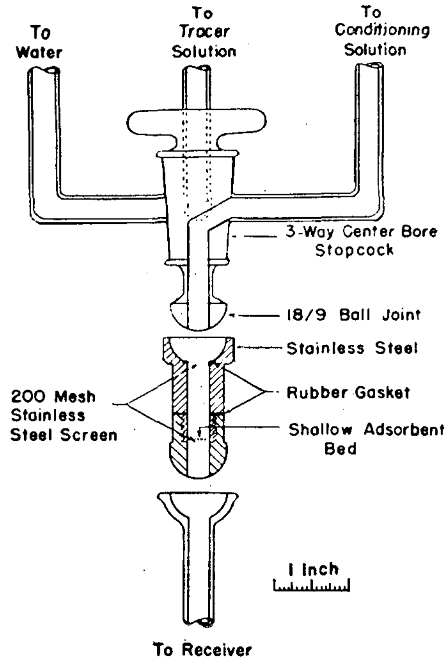

Figure 16. Experimental Arrangement for Determination of Adsorption Rates with Shallow Beds (5)

Determination of Equilibrium Constants and Activity Coefficients. Schubert (43) and Schubert and Richter (44) have utilized cation exchangers for determining the equilibrium dissociation constants of citrate and tartrate complexes of strontium by comparing the exchange equilibria for strontium in the presence of citrates and tartrates with the exchange equilibria for salts of strontium that are completely dissociated. Samuelson (34) utilized this method for determining the composition of complex phosphates of iron and others have investigated the composition of chrome liquors with exchange resins. The latter studies attempted to determine the distribution of anionic, cationic, and neutral chromium species utilizing both anion and cation exchangers. However, this procedure is subject to an error, as the equilibria among these species are disturbed on contacting an ion exchange substance. In an analogous manner Vanselow (50) has determined the activity coefficient for several ions.

Group II Precipitant. Gaddis (15) has found that a weak base polyamine-type anion exchanger when saturated with hydrogen sulfide serves as a general precipitant for the Group II cations. However, it appears that because this type of resin is not sufficiently basic to adsorb appreciable quantities of hydrogen sulfide unless free alkali regenerant is present, the use of a strong base anion exchange resin would be better. The use of such a precipitant in a column operation simplifies the qualitative analysis procedure, since it will avoid extensive hydrogen sulfide treatments and troublesome filtrations.

Precipitant for Nickel, Cobalt, Zinc, and Copper. As strong base anion exchangers are capable of adsorbing or exchanging

Table VI. Regeneration of Ion Materials

Substance	Regeneration Requirement
Sulfonic acid cation exchangers	50 milliequivalents 10% HCl per gram 50 milliequivalents 10% NH_4Cl per gram
Carboxylic acid cation exchangers	40 milliequivalents 5% HCl per gram
Weakly basic anion exchangers	30 milliequivalents 5% NaOH per gram 30 milliequivalents 5% HCl per gram
Strong base anion exchanger	50 milliequivalents 10% NaOH per gram 30 milliequivalents 10% NaCl per gram
Siliceous cation exchangers	20 milliequivalents 0.05 *N* HCl per gram 20 milliequivalents 0.05 *N* NaOH per gram

cyanide ions, it is possible to utilize the cyanide form of a strong base anion exchanger as a precipitant for such ions as nickel, cobalt, zinc, and copper. The use of the cyanide resin in a column is analogous to the previous case of the Group II precipitant.

Recovery of Valuable Analytical Reagents. In many analytical laboratories, the extensive analyses of chlorides, potassium, and sodium require large quantities of silver nitrate, chloroplatinic acid, and uranyl acetate. Of the three reagents, platinum is usually the only reagent that is recovered and the usual technique recommended for this recovery is tedious and time-consuming. There is considerable evidence (*34*) to indicate that the silver chromate and chloride of a Mohr titration can be recovered by pouring the titration mixture immediately through the hydrogen form of a sulfonic acid cation exchange resin. The precipitate dissolves and the silver is bound to the exchanger and may be eluted with calcium nitrate and the silver recovered as silver nitrate. The dissolved potassium chloroplatinate precipitates and the excess chloroplatinic acid resulting from a potassium determination may be adsorbed on the chloride form of an anion exchanger and desorbed with either hydrochloric acid and the excess hydrochloric acid removed on concentration by evaporation. The uranyl ion in the uranyl solutions and precipitates obtained in sodium analyses may be recovered with a cation exchanger and eluted as uranyl acetate with acetic acid.

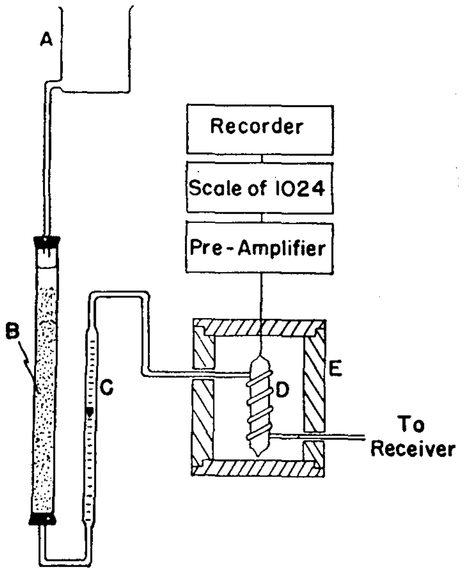

Figure 17. Experimental Arrangement for Adsorption Column Studies (*6*)

A. Solution reservoir
B. Adsorbent bed
C. Flowmeter
D. Geiger-Müller counting tube
E. Lead shield

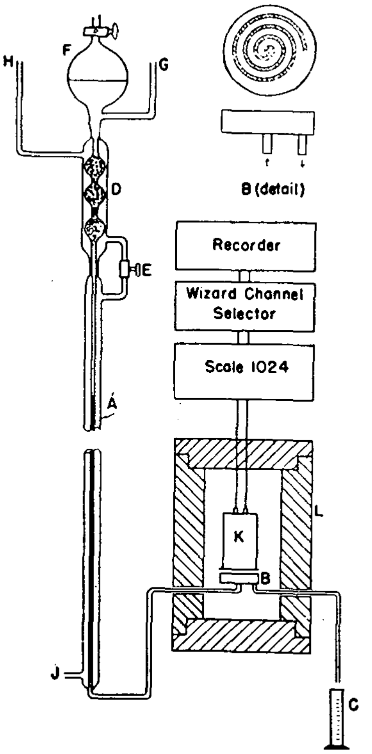

Figure 18. Experimental Arrangement Employed in Adsorption Column Separations (*20*, p. 2804)

A. Adsorbent bed, Amberlite IR-1 or Dowex-50
B. Counting cell
C. Receiver
D. Allihn condenser
E. Throttle valve
F. Gas entrainment bulb
G. Elutriant inlet
H. Thermostat fluid inlet
K. Mica end window Geiger-Müller counting tube
L. 2-inch lead radiation shield

Preparation of a Distilled Water Substitute. The use of ion-exchange substances for preparing a substitute for distilled water is a well-recognized procedure. However, the availability of new exchangers having a very low solubility and high basicity now enables one to prepare water using a small laboratory unit having a quality of 10^{-6} ohm and free of silica and carbon dioxide (*23*). In order to achieve such results, the use of a strong base anion exchanger is required for the final removal of all traces of boric, carbonic, and silicic acids.

ION EXCHANGE APPARATUS AND TECHNIQUES

Exchanger Treatment. The particle size of an exchanger is an important factor for chromatographic separations and for cases in which a separation is based upon the inability of an ion to diffuse into the exchanger particle. For the former case, a small particle is of importance and particles in the 100- to 300-mesh range have been used satisfactorily. In the latter case, particles greater than 0.5 mm. in diameter have been preferred. For all other ion exchange operations, particles having a particle size 0.3 to 0.4 mm. in diameter are ideal, in that the rate of exchange is satisfactory and a bed of these particles is not subject to any appreciable pressure drop.

The resin conditioning is of marked importance and may determine the success or failure of an analytical operation. As most analytical processes require at least a 99.9% completion of the reaction involved, it is essential that the exchanger substance be completely in the ionic form desired. Table VI contains some recommended regeneration conditions for typical ion exchange substances. These conditions are not economic values but regeneration requirements which will ensure complete regeneration. Columnar regeneration is to be preferred.

Of equal importance as particle size and regenerant conditions are the flow rates that should be maintained for satisfactory analytical performance. For chromatographic separations, it is of considerable advantage to operate as near to equilibrium conditions as practical and rates of the order 0.01 to 0.05 ml. per ml. of exchanger per minute have been found satisfactory for 100- to 300-mesh particles. However, for other analytical operations in which equilibrium conditions are not required, flow rates in the region 0.05 to 0.1 ml. per ml. of exchanger per minute are satisfactory.

Analysis of Exchangers. In many instances, the degree of regeneration or the total exchange capacity of a particular ion exchange material must be ascertained before the exchanger is to be used for analytical purposes. The determination of the total exchange capacities of clays and soils has received considerable attention since the classic work of Thompson (*47*) and Way (*51*) during the last century, and considerable disagreement exists as to a method or even the "significance" of the total exchange capacity. The difficulty in a total capacity determination for siliceous exchangers is mainly due to the fact that these substances are unstable under conditions that are en-

Table VII. Total Capacity of Some Ion Exchange Resins

Resin	% N	% S	Total Exchange Capacity	
			Theory *Me./g.*	Experimental *Me./g.*
Sulfonic acid cation exchanger	...	5.4	1.73	1.70
Sulfonic acid cation exchanger	...	8.1	2.60	2.55
Sulfonic acid cation exchanger	...	14.4	4.62	4.58
Carboxylic acid cation exchanger	...	...	...	11.0
Anion exchanger	4.0	...	2.85	2.81
Anion exchanger	14.2	...	10.1	10.0

countered during such a determination. However, commercially available organic exchangers have stable structures that will permit an accurate determination of their total capacity without degradation. In brief, the procedures involve the transformation of the exchanger to either the hydroxyl form for anion exchangers or the hydrogen form for cation exchangers. The resins are then examined by either of two methods. For strong acid and strong base exchangers, an extraction with a neutral salt will liberate a titratable quantity of acid or base equivalent to the total capacity. The treatment of the weak acid and weak base exchangers requires treatment with an excess of standard acid and base and an analysis of the amount of acid or base neutralized after equilibration. Determination of the exchange capacity of resins by the above procedure usually agrees with a chemical analysis of the active groups contained in the resin (see Table VII).

Ion Exchange Apparatus. The apparatus for utilizing ion exchange substances may be fashioned from ordinary equipment used for chromatographic analyses. However, several investigators have designed several types of apparatus that may be utilized simply and exhibit certain obvious advantages. Figure 18 illustrates a simple apparatus that may be employed for semimicrooperations and contains approximately 1 ml. of exchanger. Figures 14 to 16 illustrate apparatus designed for macro work. An apparatus designed for following the analysis of the effluent continuously by radioaction measurements is illustrated in Figures 17 and 18.

The use of ion exchange in analytical chemistry is not a panacea but it has simplified many analytical operations. As chemists become more and more acquainted with the principles of ion exchange and the properties of ion exchange substances, we may expect to find ion exchange in analytical chemistry taking its place along with chromatography and other related analytical processes.

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NUCLEONICS

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EVERY analyst is familiar with the fact that radioactive elements in all forms of chemical combination can be identified, and quantitatively determined in extraordinarily minute quantities, by measuring the kind and amount of radioactive emission of the disintegrating nuclei. The application of radiation phenomena to the study of chemical reaction has progressed very rapidly in recent years.

With the dropping of the first atomic bomb, the developments in nuclear science made in the preceding 5 years were brought suddenly to the attention of the public. Most of the vast accumulation of data had been withheld from publication and now is only slowly being released from classification. The most notable advance was the successful operation of a chain-reacting pile (*97*). This provided a source of neutrons both for the large-scale production of new radionuclides (*61*) and for the measurement of properties of atomic nuclei. The development of large facilities for the separation of stable isotopes together with the thermal neutron pile led to a sudden expansion of the number and amount of the available radioactive and stable isotopes. For isotopes not capable of production by the pile, the cyclotron is the next most important means which can produce not only all the isotopes made in the pile but many others (*55*).

This article reviews the publications of the past 2 years in the field of nucleonics that relate essentially to problems of analysis. Its three main sections deal with types of procedure, methods of measuring radioactivity, and other related matters.

TYPES OF PROCEDURE

Tracer Methods. Since the chemical properties and many physical properties of radioactive elements are substantially identical with those of their inactive isotopes, it is possible to study chemical reactions by substituting radioactive elements for all or a part of the inactive ones. By measuring the activity of the mixture it is possible to determine the processes which occur with a degree of speed and accuracy not to be hoped for from other methods. This method is generally referred to as radiochemical tracer techniques. These techniques are most extensively used in the study of physiological processes, but they also provide a powerful tool of investigation for the analytical chemist.

The simplest and most widely used method of utilizing the radioactive emission of a radionuclide (*61*) is as a tracer or tagged atom. Here the radioactive atom and its nonradioactive isotope are carried together throughout an operation, and are finally again determined by their known specific activity. For instance, in a simple case in which samples of determined specific activity were used, Thiers (*103*) and his co-workers surprisingly found that no ruthenium was lost by volatilization during the fusion and crystallization operations of the fire assay, whereas considerable ruthenium passed into the slag and the cupel. To ascertain that no ruthenium was lost by volatilization would have been extremely difficult, if not impossible, without the aid of a radioisotope. In testing the completeness of the electrolytic separation of copper from zinc, Haenny and Mivelaz (*47*), using the isotope Zn^{65}, found that 1 gram of copper was contaminated by less than 10^{-15} gram of zinc.

The simple tracer technique has been applied to the difficult problem of the separation and determination of the rare earths. Studies (*59*) on separations by ion-exchange using radionuclides brought out the superiority of Dowex 50 over Amberlite IR-1 when the activity was found to decrease to background between each band of activity in the former. In their study of the relative adsorbability of the rare earths on Dowex 50, Ketelle and Boyd (*59*) found the order La > Ce > Pr > Nd > 61 > Sm > Eu > Gd > Tb > Dy > Y > Ho > Er > Tm > Yb > Lu, with the triplet Dy, Y, and Ho as the most difficultly separable of all of the rare earths. With Amberlite I R-l, Boyd *et al.* (*16, 17*) found the order of absorption affinity was La > Y >> Ba >> Cs > Rb > K > NH_3 > Na > H > Li.

One of the most useful techniques of analysis using the radioactivity of active isotopes is that of isotope dilution, most used in biochemical investigations (*58, 84*). The method can be used in two principal ways as outlined by Henriques and Margnetti (*53*).

I. The active compound, P^*, of known amount mg_{p^*}, is added to a system containing the unknown quantity of nonradioactive compound, P. After mixing, a sample, mg_{pp^*}, of the mixed compound, PP^*, is taken and the ratio, R, of the specific activity of P^* to that of PP^* is found, when

$$mg_p = mg_{p^*}(R - 1)$$

II. The reverse procedure, usually called inverse isotope dilution, is carried out by adding a known amount, mg_p, of nonradioactive compound, P, to a system containing the radioactive compound P^* (and none of the nonradioactive compound) in a mixture of other radioactive compounds. The mixed compound, PP^*, is isolated in the pure state and the ratio, R, of the specific activities is found by determining the specific activity of PP^* and calculating the specific activity of P^* by stoichiometry from the known activity of the radionuclide. The amount of radioactive compound is then

$$mg_{p^*} = mg_p(1/R - 1)$$

A discussion of the precision of these methods is given by Radin (*84*). When all of the compound containing PP* cannot be isolated in the pure state—i.e., only an unknown fraction of the whole mixture can be used—the dilution method must be modified. Bloch and Anker (*15*) suggest using two consecutive reverse isotope dilution experiments (method II) with aliquots of different amounts of normal carrier added for the case where the original amount of the compound was too small to be isolated in pure form. The error of estimation, however, is greatly increased. An exact set of equations for isotopic dilution experiments was given by Gest, Kamen, and Reiner (*40, 58*).

Induced Radioactive Excitation Methods. A most interesting procedure, and one of limitless possibilities, is to subject ordinary materials to bombardment with various particles or forms of radiation, and thus to convert some of these ordinary atoms to radioactive ones. These radioactive atoms may be isotopes of the original atoms or they may be entirely different elements. The resulting activity is then determined by one of the usual methods for such determinations.

Sagane *et al.* (*90*) used such a method to determine sodium in aluminum. By bombarding the metal with deuterons having an energy 3 m.e.v., they were able to determine the sodium content to a limiting value of 0.001%. In this type of method, bombardment may likewise be done by neutrons or protons. For example, Von Ardenne and Bernhard (*106*) determined carbon in iron samples by measuring the activity of the isotope N^{13} which was produced from C^{12} by bombardment with 1 m.e.v. protons, as well as with deuterons. Such a method depends on the relative activation cross sections of the elements present. The term "cross section" is a way of stating the probability of a reaction's taking place. In this instance it is the probability that the bombarding particles will produce an active nuclide.

The utilization of relative activities produced by nuclear excitation is not limited to corpuscular radiation. The absorption of γ-rays by beryllium and deuterium, with subsequent production of neutrons, was utilized by Victor (*105*) in determining radium and radiothorium. The yield of neutrons produced by the action of the x-rays on beryllium and deuterium was determined by measuring the β-radiation produced in silver foil by the paraffin-slowed neutrons, and comparing the value obtained with that of a standard mixture. If the total emission of the original sample is known, the mesothorium content can likewise be found.

An interesting example of this technique was combined with the separation by ion exchange in the analysis of a sample of highly purified erbium, which gave no spectral lines of any other rare earth, for the amount of thulium present as an impurity (*59*). Processing on the Dowex 50 column after neutron bombardment gave traces of lutecium, ytterbium, thulium, and sodium besides the erbium. Assaying the thulium with a known counting geometry gave the number of Tm^{170} atoms. From the neutron cross section of Tm^{169}, the neutron flux of the pile, the time of bombardment, and the number of Tm^{170} atoms produced, the amount of Tm^{169} originally present was calculated.

This example is an illustration of the production of extraneous radioelements. Such mixtures of radioactive substances have to be separated by some means from the particular radionuclide desired. The subject of such contaminants in tracers was covered by Cohn (*19A*). Besides chemical methods of separation, two physical methods are used.

Differential decay, the simpler of these, takes advantage of the relative decay rates by letting short-lived nuclides decay to insignificant activities before measuring the activity of the nuclide under study; or more generally, measuring the activity at two or more different times. The contributions of each component are then calculated as the sum of the individual contributions

Differential Absorption. When the energies of the radiation from two (or more) radionuclides are sufficiently different, one radiation may be preferentially absorbed by some material. The other radiation of higher energy, not stopped by the absorber, then can be counted separately.

A method of analysis based on differential absorption was used by Nag-Chowdhury, Das, and Dasgupta (*76*) to determine uranium and thorium simultaneously by measuring the radiation with absorbers of different thicknesses. Nag-Chowdhury and Monsuf (*77*) estimated the uranium and thorium by means of the α-activity by comparison of the absorption curves of mineral samples with those of samples of known uranium and thorium content.

The maximum energy of the β-emission is a characteristic of the particular radionuclide. Use may be made of its determination as a means of chemical identification. The experimental techniques of two methods of its determination by absorption were given in a review by Glendenin (*41*). The simplest is the "visual estimation" from a plot of radiation detected through the absorber as a function of the thickness of the absorber. The second is a comparative method introduced by Feather (*35*).

Yaffe and Justus (*113*) using Formvar films developed a rapid method for determining the maximum energies of β-emitters. For β-emitters with simple spectra the increase in the number of counts per minute because of back-scattering is obtained as a function of the maximum energy of β-emitters. From the once established empirical relation the maximum energies of other β-emitters can be determined.

The half-life is also a characteristic of the particular radionuclide. It has been the major means of identifying new elements. The methods for measuring half-lives usually involve measuring the time decay of a sample. A variation of the usual method of decay measurement was proposed by Graves and Walker (*45*). Foils are irradiated for different periods of time and the emitted particles are counted after a time interval that has been adjusted to make the counting rates the same. These authors used indium of 54-minute half-life as an illustration of this method.

A rapid method for the determination of half-life periods of radioactive substances was suggested by Riedhammer (*87*), using a half-life value for accidental coincidences. With twofold coincidences this was shown to be equal to half the half-life of the radioactive substance.

The disintegration schemes for radioactive nuclei can be determined by coincidence counting. The apparatus and methods for obtaining such schemes were given by Mandeville and Scherb (*68*).

Besides producing new nuclides, radiation can cause chemical changes. Thus when radioisotopes are used consideration should be given to the possibility of altered valences of the compounds under analyses. A number of investigations along this line are appearing. Water irradiated by 1 m.e.v. cathode rays or x-rays was found by Allen (*2*) to be decomposed to hydrogen and hydrogen peroxide, the latter yielding oxygen. All types of radiation break up water to the free radicals H and OH, which dimerize to H_2 and H_2O_2. The concentration of hydrogen is increased by solutes, which may act by inhibiting the back reaction. Not unexpectedly, Krenz (*62*) found that the heavy particles are more effective per million electron volts than are x- or γ-rays in decomposing water.

With the loss of an electron by β-decay 19-minute LA^{143} present as La^{+++} should yield C^{++++}, unless the effects of the radiation lead to a reduction. Davies (*30*) found that over 60% of the cerium in solution was in the state Ce^{++++}. With Se^{83} and Se^{84} as SeO_3^{--} or SeO_4^{--}, the fraction of the daughter present as BrO_3^{--} was found to be 30 to 50% regardless of the original selenium isotope used, its valence state or the pH. The distribution in per cent of the valence states of iodine formed from solutions of Te^{132} was found to be:

	Valence States of I		
	+7	+5	Reduced
From TeO_3^{--}	11	14	75
From TeO_4^{--}	12	28	60

The variety and nature of the recoil excitation energy of the residual heavy nucleus from a nuclear reaction were reviewed by Libby (*65*). The first class of reactions is of processes involving no change in atomic number (Szilard-Chalmers reaction, *102*). The bond between the activated nuclide and the remaining part of the molecule is ruptured, and the activated nuclide is easily separated chemically from the parent material. Retention by the parent material is concluded to be due to recombinations. Methods for decreasing retention were summarized. The second class is of processes involving a change in atomic number. With ionic crystal targets the hot recoil particles are very short ranged. When the stable ion produced is the radioactive nuclide, baking is proposed to drive the active nuclide to the target material surface. The use of small crystals is suggested.

Willard (*110*) showed that bromine will react with liquid ethylene tetrachloride after neutron capture with a probability of 37%, and after isomeric transition with a probability of 85%, whereas in the vapor phase it will react only after isomeric transition. Williams (*111*) found that 45% of the isomeric transitions of tellurium isotopes were incapable of producing chemical change.

Methods Involving Absorption of Radiation. Direct neutron absorption enables one to examine the relative isotopic constitution of mixtures, since the isotopes of an element do not exhibit identical nuclidic properties. Moyer *et al.* (*75*), for example, determined the isotopic composition of cadmium by the absorption of slow neutrons in natural cadmium. Walker (*107*) made use of the relative absorption of neutrons to determine boron in solutions of unknown boron content by comparison with standard boric acid solutions. By an extension of their method of determining boron, involving transparency to thermal neutrons, Sue and Martelly (*101*) assayed the boron, silver, lithium, and cadmium contents of nitrate and sulfate mixtures, and in addition suggested applications of the method to the control of cadmium plating.

METHODS OF MEASURING RADIATION

Counting. The most widely used instrument for counting the particles emitted by a radionuclide is the Geiger-Müller counter with the attending scaling circuits. A review on particle and quantum counters was given by Corson and Wilson (*23*). Because the particles are emitted closely but irregularly spaced with respect to time, the question of missed counts becomes significant, especially when the counts are occurring at rates nearly equal to the relaxation times of the counter. The question of piling up of background counts in an ionization chamber was studied by Serber (*93*), who used the approximation that a count is recorded whenever the total ionization becomes greater than some given amount. Rainwater and Wu (*85*) reviewed statistics of counting.

Photomultiplier tubes are also being used as detectors for particles. Allen (*3*) used a special photomultiplier tube to record the flashes of light produced by primary particles in a fluorescent screen. A single high speed electron is sufficent to produce a pulse in the output of the tube. Designs for α-particle scintillation counting using an inexpensive 931-A photomultiplier tube have been given (*21, 96*). The phosphors (*37*) used are usually of zinc sulfide. Naphthalene was found to be less efficient than powdered sodium iodide with 0.1% thallium (*54*). This phosphor, however, is hygroscopic. Anthracene has been found to be 5 times more efficient than naphthalene for the scintillation counting of polonium-beryllium neutrons as tested by the absorption curve determined with cadmium (*12, 13, 112*).

The problem of interlaboratory uniformity in counting was investigated by Curtiss (*29*), who obtained a range of reported activities on equally active samples of from 40 to 180% of the average. He pointed out that much of the variability could have been reduced by use of β-ray standards now available from the National Bureau of Standards. Curtiss (*7, 8, 28*) gave simple instructions for the comparison of samples of isotopes differing from a given standard, and for the preparation of working standards. Knauss (*60*) pointed out that the calculation of exponential decay values is simplified by use of a slide rule.

The effect of radiation on the gases in a counter was determined by Friedland (*38*) by mass spectroscopic analysis. The vapors present in the used counter filled with ethyl acetate vapor were chiefly carbon dioxide, carbon monoxide, and methane. This increase in the number of molecules, present by the breakdown of the filling gas, is the cause of changes in characteristics of the counter. These changes, while usually allowed for, determine the lifetime of the counter.

In counting the radiation from thin films of material, two immediate troubles arise: the loss of radiation from the deeper portions of the film by absorption in the upper layers, called self-absorption, and the increase in radiation by reflection from the supporting material called back-scattering.

The variation of activity as a function of the atomic number of the backing material was found by Cowing and DeAmicis (*26*) to be a linear relation for the materials tested. Fluharty (*36*) gave the β-ray counting efficiencies for different backing materials, as determined by Peacock in 1944. The relation of back-scattering to self-absorption in β-ray measurements was investigated by Yankwich and Weigl (*120*) when the observed activities of radioactive barium carbonate samples are corrected for back-scattering it is found that their effective self-absorption corrections differ instead of being the same as for barium carbonate.

Guében, Govaerts, and Stoppani (*46*) recommend a method of correction for self-absorption using two plots: (1) observed activity as a function of total mass, and (2) log-I/μ as a function of μ (μ is the thickness of material in grams per square centimeter).

Corrections for self-absorption by thick samples were discussed by Yankwich, Norris, and Huston (*119*), who gave data for samples of $BaC^{14}O_3$ and suggested a compensation factor for geometry of counting. Armstrong and Schubert (*9*) determined the curve of relative activity of various thicknesses of barium carbonate of uniform specific activity and found that above 20 mg. per sq. cm. it is constant.

The exchange of the radioactive material with the surroundings while stored is another source of error in counting samples. Armstrong and Schubert (*10*) found that a sample of barium carbonate lost 2.7% of the original activity in 6 days. No loss of radioactivity by barium carbonate was found to occur in the absence of water vapor or carbon dioxide. Yankwich (*118*) found that a sample of barium carbonate prepared by filtration and allowed to stand for 56 hours in carbon dioxide moistened by distilled water lost 33% of its activity, but that heat-dried samples lost less than 0.7% of the activity and can be stored for long periods without serious loss of activity.

The effect of geometry on determinations with a single counter led Davis (*31*) to devise a scheme using several (4) Geiger counters in a circular arrangement about a radium source for the determination of its radium content. The arrangement gives a counting rate approximately independent of the position of the source if it is near the center of the circle.

The Electroscope. Although Geiger-Müller counters are the most widely used measuring instruments for particle detection, probably the simplest and least expensive quantitative method for radioactivity determinations is that given by Henriques *et al.* (*49*), in the first of a series of papers in INDUSTRIAL AND ENGINEERING CHEMISTRY, ANALYTICAL EDITION.

A Lauritzen electroscope was modified to place the sample inside the electroscope chamber. With this arrangement the sensitivity to the weak β-emitter S^{35} was about the same as for best designed bell-type Geiger counters. The sample is precipitated onto filter paper by having the filter paper clamped between a special fritted support and precipitation chamber. For counting, the paper is then placed in a support and clamped on with a slip-on ring. MacKenzie and Dean (*66*), in the measurement of the specific activity of phosphorus, cement the filter paper to an aluminum ring and filter the precipitate onto the assembly while clamped between the precipitation chamber and fritted-glass support. For finer precipitates, a Selas 2001 crucible (*50*) is adapted by grinding to a disk, which can then be inserted in place of the paper in the filtration assembly.

For gaseous samples Henriques and Margnetti (*51*) designed a quartz ionization chamber mounted on the Lauritzen electroscope with a collecting wire through the wall to the repelling post of the electroscope. With such a chamber the determinations of specific activities of gaseous C^{14} samples were equally as good as those obtained with a Geiger counter (3×10^{-5} μc. of C^{14} in 20 millimoles of carbon dioxide, 4 grams of barium carbonate). Henriques and Margnetti (*52*) also used this arrangement for the determination of H^3 when in the form of H_2.

Armstrong and Schubert (*10*) used a perforated brass tray as a Büchner funnel for filtering the precipitated radioactive material. Counting was done with the sample precipitate left intact in the dish. Abers (*1*) modified pressed aluminum or copper dishes (originally used for the evaporation of aliquots of solutions for counting) by drilling or punching small holes to form inexpensive Büchner-type funnels.

Photographic Methods. Quantitatively the use of photographic emulsions involves either density measurements of the exposed regions or counts of recorded tracks (*11*). The use of density measurements was illustrated by Branson and Hansborough (*18*) by means of Agfa triple S Pan film with a 14.7-day exposure to 1.38 to 2.4 μc. of P^{32} (a β-emitter without γ-emission) in a chick embryo. Development to a contrast ratio of unity ($\gamma = 1$) leads to the relation

$$\log I_0(2) - \log I_0(1) = D_2 - D_1$$

Most investigations involving particle track determinations require special photographic plates together with special development techniques (*24, 27, 33, 34, 109*). Discrimination by the plate between the types of radiation received is desirable. An elon-hydroquinone developer (D-19b) gave no discrimination between α-tracks and fission tracks, whereas a diluted p-aminophenol developer solution was found by Stevens (*99*) not to develop the α-tracks. This same effect was obtained somewhat differently by Perfilov (*80*), who used a diluted chromic acid bleach before development.

The spontaneous occurrence of α-tracks in photographic emulsions produces a background which increases with the storage time of the film before use. Yagoda and Kaplan (*114–117*) found that treatment with moisture vapor accelerates the fading of the latent image of α-particle tracks. Storage over 3% hydrogen peroxide solution at 25° C. for 4 hours and restoration of sensitivity by desiccation for 1 to 2 hours over calcium chloride was found to be applicable to Eastman NTA and Ilford concentrated emulsions.

Joliot-Curie (*56*) suggested a photographic method for the determination of total uranium and thorium content of rocks by the study of the individual trajectories of α-rays in a photographic emulsion. Poole and Bremner (*81*) used this method but obtained no conclusive results on a quantitative basis.

In the study of the radioactivity of samarium, Lattes, Samuel, and Cuer (*63*) placed a sulfate solution of the active material on the emulsion and air-dried it. After 20 days the film was washed before developing and fixing. Alpha-tracks were counted under high magnification and the half-life was determined. While the area observed is not uniform, the value of 0.93×10^{12} years was obtained, which shows the possibilities of the method.

A method for measuring the distribution and concentration of β-emitting tracer elements in a sample by means of a single magnetic lens system for the focusing of the β-rays onto film was devised by Marton and Abelson (*70, 71*). In contact radioautography the film pressed against the active surface receives

β-rays in all directions from the sources, whereas in the electron magnifier the extremely divergent rays are shielded from the film and only those focused by the lens are used. Hence, the resolution of the image on the film is improved manyfold.

OTHER ITEMS RELATED TO ANALYSIS BY RADIOACTIVE EMISSION

Neutron Sources and Reactions. The capture cross sections (relative probability for capture) for slow neutrons were determined by Coltman and Goldhaber (*20*), who used neutrons from a radium-beryllium source slowed by paraffin. Seren, Friedlander, and Turkel (*94, 95*) determined the thermal neutron activation cross sections of 67 elements and found a range from 4×10^{-7} to 725 barns (1 barn = 10^{-24} sq. cm), for the production of 31-second O^{19} and 140-minute Dy^{165}, respectively. The compilation of neutron cross sections of 54 elements by Goldsmith, Ibser, and Feld (*42*) is the most complete summary available to date.

Other than from a pile, the most convenient source of neutrons is from α-Be and α-D sources. Because different sources for the α-particles yield α-particles of different average energies, the neutrons produced also have different energies. In 1938 Ollano (*78*) studied the neutron yield from a radium-beryllium source and found the neutron yield to be 83% of that from a radon-beryllium source. Two reasons were given for the difference: the smaller energy of α-particles from radium and the closer contact between radon gas and the beryllium as compared to the mixed radium and beryllium. Hanson (*48*) compared the energy of photoneutrons from several sources with those of known energy produced from lithium by the *p, n* reaction. The sources were mesothorium-deuterium, mesothorium-beryllium, yttrium-beryllium, lanthanum-deuterium, and antimony-beryllium, which produced neutrons of maximum energies of 223, 830, 162, 174 and 26 m.e.v., respectively. The yields of neutrons from photoneutron sources were determined by Russell, Sacks, Wattenberg, and Fields (*89*) for Na^{24}, Mn^{56}, Ga^{72}, In^{116}, and La^{140} with beryllium or deuterium oxide. The highest yield was for Na^{24} with deuterium oxide, which gave 29×10^4 neutrons per second per curie of activity 1 cm. from 1 gram of target material.

Health Hazards. The hazards of radioactive material have led to the formulation of rules and procedures (*4*) for the handling of such material. K. Z. Morgan (*88*) gave a summary table of some of the tolerance values for 16 nuclides, based on the maximum permissible exposure to radiation adopted on the plutonium projects.

A table for the quick estimation of shield thickness for temporary shielding against gamma rays was prepared by C. C. Gamertsfelder (*79*).

The question of the safe handling of radioactive solutions in the usual chemical manipulations was investigated by Cowing and DeAmicis (*25*). Using a 125-ml. Erlenmeyer flask containing 100 ml. of radioactive phosphorus solution, they found that if the rate of 12.5 mr. per hour is considered a permissible dosage, the maximum time of handling the flask when containing 1 mc. of P^{32} would be 8.5 minutes. They give graphs for the handling time as a function of concentration of P^{32}.

As a final check on the amount of radiation received, some form of exposure meter should be worn, attached to the body of the investigator. The technique of using x-ray film for the measurement of exposure to low intensities of x-rays, γ-rays, and β-rays was given by Morrison (*74*).

General References. The general subject of the preparation and measurement of isotopes has been presented in a number of books and symposia. The prewar literature was summarized by DeCew (*32*). In the past year there were several texts of interest to analysts (*5, 14, 19, 22, 58, 64, 67, 86, 88*) and several charts of the properties of the nuclides were published (*39, 57, 92*). The 1947 summary of nuclear data by Way *et al.* (*108*) brought up to date the earlier compilations (*6, 42, 43, 72, 73, 91*).

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INDICATORS

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QUITE generally an indicator in chemistry is a substance which indicates the presence of a certain constituent. In this sense all the reagents which are used for the detection of a given constituent are indicators. In a more limited sense an indicator is a substance which indicates the extent to which a reaction between two or more reactants occurs. In volumetric analysis the selected indicator should indicate the point where the reaction between the reactants has become stoichiometric. If this condition is fulfilled the visual end point in the titration coincides with the equivalence or theoretical end point.

ACID-BASE INDICATORS

Acid-base titrations have remained confined mainly to those in aqueous medium or in mixtures of water and some water-soluble organic solvent. Of late, titrations in nonaqueous aprotic solvents have become of some importance, partly for theoretical reasons in connection with theories of acids and bases and partly for analytical purposes. Titrations in aprotic solvents will have a limited analytical applicability, because most salts of inorganic cations and inorganic or organic anions are insoluble in such solvents. Titrations in aprotic solvents probably will remain confined mainly to the titration of organic bases with organic Brönsted acids or Lewis acids. Considering the wider scope of application of acid-base indicators their definition may need some revision. As long as aqueous solutions are being considered the time honored definition, that an indicator is a weak acid or a weak base whose dissociated form has a different color from the undissociated form, can be maintained. Considering the wider scope of application of acid-base titrations the following revised definition is proposed: Acid-base indicators are weak acids or weak bases, the acid form of which has a different color from the basic form.

This definition satisfies the behavior of indicators in protic and aprotic solvents. In aprotic solvents the reaction product of an indicator base (I_b) and a Brönsted acid (HB) has the color of the acid form of the indicator, although under the above conditions the degree of dissociation of the reaction product is usually small. The same is true of the reaction product BHI of a Brönsted indicator acid HI and a base B. Davis and Schuhmann (*6*) state that "there is strong evidence that in a partially substituted ammonium salt, non-Coulombic interaction occurs between the negative ion and the proton of the positive ion in nonaqueous solvents. In other words, a hydrogen bridge is formed between the cation and the anion. It seems to be fairly well established that in salts of the type *BHOR* the hydrogen bridge is strong, even in a solvent of relatively high dielectric constant." Actually the statement that there is a hydrogen bridge (bond) between the cation and the anion is not quite exact. As a matter of fact the reaction product of an acid and a base which have combined by the formation of a hydrogen bond may be more or less completely un-ionized like the reaction product of ammonia and water.

The proposed definition also satisfies the behavior of an indicator base toward a Lewis acid. The neutralization product of the base and the acid has the color of the acid form of the indicator. In his classical studies, G. N. Lewis mentioned that an indicator base, like dimethylaminoazobenzene, changes color from yellow to red by the addition of acids like boron trifluoride, antimony trichloride, etc. It may be expected that ordinary acid-base indicators will find more application in the future in the titration of Lewis acids with bases in aprotic solvents.

Aqueous Medium. There is a host of substances which are useful as acid-base indicators in titrations in aqueous medium. If the color change at the end point is not very pronounced, use often can be made of suitable mixed indicators which give a sharper color change at the end point than unmixed indicators (*5*). It should be mentioned also that an interesting study of the luminosity, dominant wave length, and spectral purity of indicators in relation to the visual detection of end point has been described (*29*).

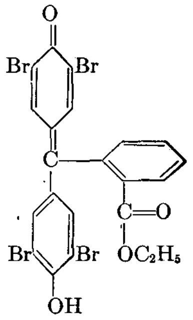
Some new substances have been added to the long list of existing indicators for aqueous mediums. A few of the new indicators are given in Table I.

A new type of acid-base indicator for aqueous solutions was described by Hirsch (*14*). He added to the aqueous solution a small amount of lead acetate and a few milliliters of carbon tetrachloride containing dithizone. Under the experimental conditions employed most of the lead remained in the aqueous phase if the pH of the solution was less than 4. The color of the carbon tetrachloride phase was therefore green (dithizone) at a pH less than 4. However, if the pH was greater than 4 some of the lead was extracted into the organic phase causing the color to change from green to red (lead dithizonate). Hirsch suggested that this indicator would be useful in titrating a colored aqueous solution provided that the colored components are not extracted by carbon tetrachloride. It appears that the indicator is of little practical value for this purpose because traces of various metals in the aqueous solution would interfere seriously. However, the principle underlying the use of the indicator is interesting.

Table I. New Acid-Base Indicators for Aqueous Solutions

Name	Acid Color	Basic Color	pH Interval	pK (if Given)	Literature Cited
p-Dimethylamino-*p*′-azobenzenesulfonamide	Red	Yellow	3 to 4.5	. . .	(*28*)
Disodium 4,4′-bis(*p*-dimethylaminophenylazo)-2,2′-stilbenedisulfonate	Orange-Red	Blue-Violet	4.0 to 5.4	. . .	(*27*)
Disodium 4,4′-bis(o-tolyltriazeno)-2,2′-stilbenedisulfonate	Yellow	Muddy	Approx. 4 to 5	. . .	(*27*)
Disodium hydroxymercuridibromofluorescein (mercurochrome)	Red	Fluorescent	. . .	Approx. 4.5	(*1,7*)
1,3-Bis(3-methyl-4-nitro-5-pyrazole)-triazene	Colorless	Orange	Approx. 7 to 8.5	. . .	(*20*)
Ethyl-bis-2,4-dinitrophenyl acetate	Colorless	Blue	7.4 to 9.1	8.3	(*11*)
Disodium 2-(4′-nitrophenylazo)-1-naphthol-4,8-disulfonate	Pink	Purple	Approx. 8 to 10	9.6	(*12*)
Disodium 2-(2′-methoxy-4′-nitrophenylazo)-1-naphthol-4,8-disulfonic acid	Pink	Purple	Approx. 9 to 11	10.0	(*12*)
Disodium 2-(4′-nitrophenylazo)-1-naphthol-3,8-disulfonic acid	Pink	Purple	Approx. 11 to 13	12.0	(*12*)

Nonaqueous Medium. Knowledge of acid-base indicators in nonaqueous mediums and especially in aprotic solvents is very limited. Many of the indicators useful in aqueous solutions cannot be used in a solvent like benzene. Davis and Schuhmann (*6*) state that before acid-base measurements of organic solutions can be performed as readily as those of aqueous solutions, it will be necessary to provide a series of indicators ranging from strongly acidic to strongly basic compounds. Davis and Schuhmann prepared the following new indicators: ethyl ester of tetrabromophenolphthalein designated as bromophthalein magenta E, and tetrabromophenolphthalein *n*-butyl ester, called bromophthalein magenta B. The magenta E has the structure:



The solid can be ground to a brick-red powder which melts to a deep-red liquid at about 209° to 210° C. The compound gives a yellow solution in benzene, cyclohexane, dioxane, ethyl acetate, and ethylene dichloride. The product of its reaction with secondary aliphatic amines or tetraalkylammonium hydroxide gives blue solutions in benzene, while tertiary aliphatic amines and symmetrical di- or triaryl substituted guanidines react with bromophthalein magenta E to give magenta solutions and with primary aliphatic amines to give red-violet solutions. The difference in color is attributed to differences in the strength of the hydrogen bond and to dimerization. For example, the purple-blue salt with a secondary amine in benzene is considered a dimer which is stabilized by resonance.

The relative strengths K_b of some organic bases towards magenta in benzene was determined quantitatively. K_b is defined by the expression

$$K_b = (S)/(B)(A)$$

in which S is the reaction product *BHOR*, and A the indicator acid *HOR*. The following pK_B (= $-\log K_B$) values are reported: *n*-dibutylamine 4.19; triethylamine 4.36, piperidine 5.08, diphenylguanidine 5.35, ditolylguanidine 5.80. Thus the guanidines are the strongest bases in this series.

The reaction of bromophthalein magenta with organic bases in cyclohexane and ethylene dichloride also was investigated by Davis and Schuhmann, while qualitative observations are reported in quite a number of other solvents, like toluene, carbon tetrachloride, carbon disulfide, partly halogenated hydrocarbons, ethers, esters, ketones, and alcohols.

Davis and Schuhmann performed successfully in benzene the titration of 0.005 M *d*-camphorsulfonic acid with 0.01 M diphenylguanidine, of 0.0025 M dicyclohexylguanidine with 0.005 M camphorsulfonic acid, of 0.05 M di-*o*-tolylguanidine with 0.1 M trichloroacetic acid, of 0.01 M solution of the same base with

0.01 M picric acid and of 0.1 M and 0.01 M triethylamine with 0.1 M and 0.01 M, respectively, trichloroacetic acid. In all these titrations bromophthalein magenta gave a sharp reproducible end point. The indicator is a relatively strong acid (similar to bromophenol blue in water) and it cannot be used in the titration of acids as weak as benzoic and acetic acids.

INDICATORS FOR OXIDATION-REDUCTION REACTIONS

Smith and Richter in 1944 prepared a number of derivatives of 1,10-phenanthroline (*22*) and studied the properties of the ferrous complexes of the phenanthroline derivatives (*4, 24, 25*). The complexes, which are similar to the familiar ferrous phenanthroline, were found to be sensitive and reversible redox indicators. However, their use appears to be limited mainly to titrations with ceric ion because of their high oxidation potentials (1.0 to 1.3 volts in 1 M sulfuric acid). The 1,10-phenanthroline ruthenous and the bipyridyl ruthenous ions also have been investigated as indicators (*8, 26*). (The color change is from red in the reduced form to pale blue in the oxidized form.) The oxidation potential of these complex ions is also high, about 1.3 volts.

It should be mentioned that studies of the dissociation equilibria of the ferrous and ferric phenanthroline complexes have been described recently (*9, 16*). In addition, a study of the kinetics of formation and decomposition of the two complexes has been made (*17*). From these studies the stability of the indicator in acidic solutions is known.

The reversible diphenylamine indicators, which are very useful in titrations in acid solution, have been shown by Willard and Manalo to be adaptable to titrations in alkaline media (*30*). Thus diphenylamine sulfonic acid and 2-aminodiphenylamine sulfonic acid-4 were found satisfactory for the titration of arsenite with hypobromite in alkaline solution. Diphenylamine sulfonic acid, 2-carboxy-2′-methoxydiphenylamine, 2-carboxy-2′-methyldiphenylamine, 2-carboxy-diphenylamine, and 2,2′-dicarboxydiphenylamine were found to be useful for ferricyanide titrations in alkaline solutions. The color changes were found to be reversible provided that solutions containing the unstable oxidized forms were not allowed to stand for too long a period of time.

Knop and Kubelkova (*15*) introduced n-methyl diphenylamine-p-sulfonic acid as a redox indicator. The mechanism of the color change is comparable to that of diphenylamine; the color of the oxidized form of the indicator is bright red. Eeckhout and Tavernier (*10*) determined the absorption spectrum of the red form (maximum absorption at 5100 Å.), its stability and the oxidation potential of the indicator. In a medium with an acidity between 0.01 to 1 N sulfuric acid the normal potential is reported to be 0.81 volt (*vs.* N - H_2 - El.).

Three new reversible redox indicators of the phenazine type have been described by Albert and Duewell (*3*). The indicators are 1-hydroxyphenazine (E_0 = 0.18), 1-aminophenazine (E_0 = 0.18), and 1,3-diaminophenazine (E_0 = −0.28). These indicators with very low oxidation potentials have not yet been used in titrations.

In addition to the reversible indicators mentioned above a few nonreversible indicators have been suggested for titrations with strong oxidizing agents. α-Naphthol has been used in the titration of iron with dichromate solution (*2*). Cresyl violet (an oxazine dye) can be used for titrations with hypochlorite (*23*). Several of the indicators tested by Willard and Manalo (*30*) can be used also for titrations with hypochlorite and hypobromite in alkaline medium. There still exists a need for new reversible indicators that can be used in titrations with bromine, chlorine, hypobromite, hypochlorite, and chloramine T.

INDICATORS FOR IODOMETRIC TITRATIONS

Starch is still the time-honored indicator for iodine. However, it has the disadvantage that the starch iodine adsorption complex is only slightly soluble in water. It is for this reason that starch should not be added to a solution containing more than a small amount of iodine. A new indicator for iodine which does not have this disadvantage (*21*) (the sodium salt of starch glycolic acid) has been described. The procedure for preparing the sodium starch glycolate from starch is lengthy. However, the new indicator may eventually be commercially available.

Amylose has been suggested as a substitute for starch because it gives a sharper end point in iodometric titrations (*18*).

ADSORPTION INDICATORS

No striking new developments in this field have been published in recent years. A new adsorption indicator, p-dimethylaminobenzylidene rhodanine, has been suggested for the titration of chloride and of bromide with silver (*13*). Another new adsorption indicator is succinylfluorescein (*19*). This compound is similar to fluorescein in properties and can be used for the argentometric titration of chloride, bromide, iodide, and thiocyanate in neutral solution but not in acid solution.

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FLUOROMETRIC ANALYSIS

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IN A review of fluorescent analysis as applied to inorganic material appearing in this journal in 1939 (*117*), several books devoted to this subject were mentioned. Some of these have been revised and serve as excellent references.

Danckwortt's book (*20*) which is specifically concerned with analysis in ultraviolet light, was revised in 1940 and has appeared in this country in lithoprinted form. This contains 1583 references. Feigl (*29*) gives many fluorometric applications for organic as well as inorganic compounds. Radley and Grant (*92*) also have an enlarged third edition; Chapter 8 which is on inorganic analysis has 123 references. Texts dealing with colorimetric analysis almost invariably give a discussion of fluorometric techniques. Sandell (*100*) gives methods for several elements and the Snells (*107*) in Chapter 15 of their third edition cover some general principles and apparatus for fluorescent analysis. Because of the listing of the fluorescent color of many substances—for example, 2896 organic compounds—the analyst will be interested in DeMent's book (*22*); however, the review by Fonda (*33*) should be read in connection with this. From a theoretical standpoint the Cornell symposium papers on solid luminescent materials edited by Fonda and Seitz (*34*), and the paper by Kasha (*55*) are of interest.

APPARATUS

Lamps. Many of the commercial manufacturers—for example, General Electric, Westinghouse, Sylvania, Hanovia Ultraviolet Products Inc., and Cooper Hewitt—produce lamps for the specific purpose of exciting fluorescence. An interesting review of fluorescent lamp developments has been given by Neumann (*83*). A discussion of the lamps used for fluorescent analysis in England has been given by Radley (*91*). Most recent developments in this field include the production of phosphors which when excited by short ultraviolet rays give off longer rays in the ultraviolet. A phosphor designated as 360 B-L converts the 2537-Å. mercury radiation to energy between 3000 and 4000 Å., with relatively little radiation in the visible spectrum. Lamp tubes of this type are now available similar to those used in the ordinary fluorescent desk lamp and are made with both clear and blue glass. These lamps have an advantage over the high pressure mercury vapor lamps, in that they can be turned off and on instantly without waiting for a cooling period. This subject is treated by Forsythe and Adams (*36*).

The relatively low priced germicidal lamps produced by the lamp manufacturing companies in several styles are potential sources of the 2537 Å. mercury radiation and should find application in analysis.

Fluorometers. The fluorometers of the type of the Coleman, Pfaltz and Bauer, Klett, Photovolt's Lumetron, and Hilger's Spekker have been used successfully for many years. More recent are the Fisher Scientific Company's instrument for fluorometry, the fluorophotometric accessory for the Beckman spectrophotometer, and the Farrand photoelectric fluorometer. In the latter, the fluorescent beam is directed by a lens system to the cathode of a photomultiplier tube. This seems to be one of the first commercial instruments built especially for measuring the fluorescence of solutions using this type of tube. The Photovolt Corporation has available for use with its Model 512 electronic photometer a search unit containing a photomultiplier tube which is especially adaptable for measuring the light from weakly fluorescing solids.

Many workers have found it desirable to build fluorometers of their own design or to add attachments to existing instruments. Fletcher (*32*) and others describe in detail the construction of an attachment for the Beckman spectrophotometer which permits the accurate measurement of solution with a very weak fluorescence. Lowry (*73*) has made a modification of the Coleman Model 12 photofluorometer where he has substituted an R.C.A. photomultiplier tube No. IP 21 in place of the phototube of the instrument. By using with this a special solution holder, as little as 0.1 millimicrogram quantities of riboflavin in 0.5 ml. of solution are accurately determined. Hilton (*47*) describes a micromethod for vitamin B_1 assay using a Spekker photoelectric fluorometer with a galvanometer and replacing the usual glass cell with a capillary tube. Krebs and Kersten (*68*) describe in detail for home construction a fluorometer using vacuum photocells. Fryd and Rose (*37*) have devised a simple arrangement for measuring the fluorescence of both solids and liquids using a photoelectric cell with a microammeter. The solid is placed on a glass platform and the liquid is placed in a cell on the platform. De Vore (*25*) has constructed a photometer for measuring the brightness of fluorescent pigments using the R.C.A. photomultiplier tube IP 21. A method of calibration of the tube and necessary filters are also described. This instrument should find use in the determination of uranium where the fluorescence of the solid sodium fluoride melt is measured. Carlson (*16*) and others give details for making a sensitive photoelectric photometer for measuring low fluorescent intensities. Koch (*57*) describes a simple fluorometer of the Duboscq type. Kortüm and Finclsh (*65*) give a photographic method of recording quantitatively comparable fluorescent spectra. For measurements of fluorescent spectra, Dutton and Bailey (*26*) have modified the Cenco spectrophotometer.

In order to compare the performance of commercial fluorometers in the thiochrome assay for vitamin B_1, Loofbourow and Harris (*72*) carried out an extensive series of experiments using five different instruments. They concluded that all were satisfactory. Wokes (*123*) and others give a good general discussion on the calibration of fluorometers especially for estimating vitamins, alkaloids, etc. The general principles of fluorometer design, including filters, solution cells, and photocells are outlined by Bowen (*8*). Bowen (*9*) points out that in the fluorometers using photomultiplier tubes greater attention must be paid to curvette design and to light filters, since the selective factor of the phototube will be missing and much lower intensities will affect the tube. The interference filters which are marketed by Baird Associates and are discussed by Hadley and Dennison (*45*) should be helpful in this respect and should find much use in fluorometric analysis.

It is often desirable in developing quantitative methods to measure the spectral energy distribution of the fluorescent light. The photographic method with the spectrograph has been a tedious process because of the long exposure required. Recently Studer (*109*) has described an instrument where he uses, as a receiver, a photomultiplier tube IP 22 with a standard constant deviation spectrometer for measurements of this kind. Burdett and Jones (*15*) have made an attachment for the Beckman spectrophotometer for measuring fluorescent spectra, which should find many applications. A precaution in using this modification is given by Sambursky and Wolfsohn (*98*).

Standards. Quinine sulfate, sodium fluorescein, and other compounds which fluoresce in solution are used as standards in fluorometric analysis and have many advantages. However, for routine work in setting instruments, glass standards have proved very useful. Loewenstein (*71*) has prepared glass standards for various wave bands from 3950 to 6290 Å. with fluorescent intensities corresponding to several concentrations of riboflavin and thiamine. Fletcher (*31*) and others have described the preparation of glass standards for use in the analysis of beryllium.

INORGANIC APPLICATIONS

Aluminum. Several new reagents which give qualitative fluorescence tests for aluminum have been reviewed by Radley (*87*). These are chiefly azo dyes where hydroxy groups are adjacent to the azo linkage. In most cases the fluorescence is vivid, and very low concentrations may be detected. The quantitative determination of aluminum by fluorescence has been accomplished by using the reagents morin (*118*), quercetin (*21*) (an isomer of morin), and Pontachrome Blue Black R (*7, 116*). The first two of these are not specific and the fluorescence intensity is subject to temperature changes. The Pontachrome Blue Black R gives a similar fluorescence only with gallium and has found application in the determination of as little as 0.001% aluminum in steel and bronzes (*116*).

Beryllium. Because of wartime interest the analytical chemistry of beryllium has developed rapidly. After 1-amino-4-hydroxyanthraquinone (*119*) was shown to be a good specific qualitative reagent for beryllium, Hyslop (*52*) and others employed this and 1,4-dihydroxyanthraquinone (quinizarin) for the quantitative determination of beryllium in animal tissue. These investigators obtained excellent results with visual comparison and proved the method rapid and accurate. The same reagents have been shown to be applicable for the determination of beryllium in ores (*30, 31*) and other materials (*18*). This method is especially useful in the analysis of ores, for in many cases no separations are required. The ore is fused with a sodium carbonate–borax glass mixture, this is dissolved in hydrochloric acid, diluted, and the reagent added for a direct determination. Morin (*100, 113*) has also been employed in the analysis of beryllium but it lacks the specificity of the above reagents.

Boron. Over a period of some years Neelakanatam and Row (*82*) and their associates have published the results of a series of investigations on the reactions of boric acid with *o*-hydroxycarbonyl compounds and their application in analytical chemistry especially for detecting boron and conversely identifying the organic group. Some of these compounds—for example, resacetophenone—serve as good qualitative reagents for boron if used in concentrated sulfuric acid solution. Radley (*89*) has shown that 1-amino-4-hydroxyanthraquinone will give an intense orange-brown fluorescence with boron in concentrated sulfuric acid, and is a good qualitative reagent. Benzoin (*121*) serves as both a qualitative and a quantitative reagent for boron, and has the advantage that the fluorescence is produced in an alcohol solution, eliminating the necessity of the concentrated acid. As little as 0.2 microgram of boron can be determined with this reagent.

Uranium. For many years the method of detecting uranium by fusing compounds and ores with sodium fluoride and examining under ultraviolet light has been well known. An extensive review of this procedure has been published recently by Northup (*85*). Rodden (*94*) has reported that this procedure may be adapted to the quantitative determination of uranium. The uranyl nitrate is extracted with a suitable solvent which is then evaporated and the residue fused with sodium fluoride and carbonate in a gold dish. The solid is removed from the dish and brought under an ultraviolet lamp where the fluorescent intensity is measured with a Photovolt electronic photometer. Because of the intense fluorescence of uranyl salts when activated by wave energies below 3000 Å., they may also be determined in solution. Sill and Peterson (*103*) have developed this into a quantitative method; and in order to avoid the use of quartz containers they irradiate the solution from the top of the beaker. A visual comparison is made with standards and good results are obtained.

Gallium. Most of the reagents that show a fluorescence with aluminum will give a similar but weaker result with gallium (*87*). Sandell (*99*) has shown that the 8-hydroxyquinoline complex with gallium may be extracted with chloroform and used in the quantitative determination. Indium gives a similar reaction, but may be controlled by the hydrogen ion concentration or by extracting the gallium chloride with ether, in which the indium chloride is insoluble.

Zinc. A specific qualitative test for zinc (*120*) is given by the complex which zinc forms with benzoin in an alkaline solution in the presence of magnesium ions. Apparently, the green fluorescing complex is adsorbed on precipitated magnesium hydroxide. Merritt (*76*) has developed a quantitative method where zinc is precipitated as a colloid by 8-hydroxyquinoline in the presence of gum arabic. The fluorescence of the colloid is measured with a photofluorometer.

Other Elements. In addition to the fluorometric methods given above and in the general references mentioned the following are of interest:

A specific test for thorium (*119*) is given by the reagent 1-amino-4-hydroxyanthraquinone if used in a slightly acid solution.

Iodine (*46*) may be determined in concentrations as low as 2 micrograms by mixing it with a standard fluorescein solution and measuring the residual fluorescent intensity. The diiodofluorescein formed does not possess fluorescence.

Ammonia (*112*) may be determined qualitatively by soaking filter paper in a neutral solution of zinc sulfate and 8-hydroxyquinoline and placing this in the presence of ammonia fumes. The zinc complex is not fluorescent until it becomes alkaline. The test will detect the gas from 1 microgram of ammonia in 5 ml., which is more sensitive than litmus.

A quantitative test for traces of oxygen dissolved in water is described by Konstantinova-Shlezinger (*64*) where the fluorescent intensity produced by adrenaline solutions is proportional to the oxygen present. As little as 1.8 micrograms of oxygen in 1 ml. of solution can be determined. This same author (*63*) had previously developed a test for ozone in air samples which depended on the oxidation of dihydroacridine to the fluorescing acridine. Goto (*42*) has shown that the filter paper strip method of testing for ions may be applied to the analysis of aluminum, cadmium, zinc, magnesium, calcium, zirconium, and beryllium by impregnating the paper with aluminum hydroxide and then dipping it into a solution of the ions. The paper is then developed with oxine. Goto (*43*) has been a very prolific publisher on qualitative fluorometric tests for the metallic elements. In many cases the reagents are fluorescent chemicals and the metal ion destroys this. While these tests are not specific, they do represent a great amount of experimental work and the reports serve as a real addition to the literature of fluorescent analysis.

Indicators. As indicators for acid base titrations and for particular hydrogen ion concentrations, fluorescent materials have been in use for many years (*92*). Some of these have sharp end points and change to colorless nonfluorescing forms. A review of this is given by Déribéré (*23*) and some new indicators are listed by Koesis and Pettko (*59*). Koster (*66*) suggests the potassium salt of 1,4-dihydroxybenzenedisulfonic acid as an acid-base indicator. This changes at a pH between 6 and 7 from bright blue in alkaline to nonfluorescent in acid. Koesis (*58*) shows that fluorescent indicators can be used for titrations of lead and mercury and Goto (*44*) recommends dyestuffs as rhodamine B and fluorescein, etc., as oxidimetric indicators.

FLUORESCENCE IN ORGANIC ANALYSIS

Other than in vitamin determinations and certain biological applications which are to be given in another part of this paper, the use of fluorescence in actual organic analysis has not been greatly developed. However, the spectra of the fluorescence of many individual organic compounds have been determined and applications are certain to follow. Gilman (*39*) describes a simple device for detecting fluorescence in a drop of liquid and states that of 360 compounds tested, 317 showed some fluoresence. Unfortunately, the compounds were not listed.

Radley (*90*) discusses some recent advances in fluorescence analysis with reference to organic compounds and gives details for anthranol as a reagent for glycerol. This same author has devised a test for formaldehyde (*88*) by having it react with acenaphthene-5-carboxylic acid and lists the results of other compounds with the same reagent.

Seaman (*102*) and others have shown that as little as 0.05% *o*-nitrophenol can be detected in *p*-nitrophenol by suitable reactions and fluorometric measurements. Similar results were obtained with the aminophenols.

The identification of compounds such as 3,4-benzopyrene, chrysene, anthracene, etc., by fluorescent spectrography is advocated by Berenblum and Schoental (*3*). Since oxygen (*79*) is an effective quenching agent for many of these compounds, their quantitative determination requires specific conditions. In a review on the routine analysis of crude drugs, Hopkins (*49*) shows that fluorescence methods have many applications.

Capillary fluorometric analysis by means of filter paper strips has been treated in some detail by Germann and Hensley (*38*). These authors absorb several organic compounds such as pyrene, fluorene, and salol from acetone and chloroform solutions and use a photometer of their own construction for measuring the fluorescence.

The examination of adsorption columns, used for the separation of organic compounds, with ultraviolet light has become general practice. Norberg (*84*) and others showed that this technique could be used to separate quantitatively such closely related products as tri- and tetramethyl glucose. Kirchner (*56*) and others have carried out the separation of a number of acid mixtures whose *p*-phenyl phenacyl esters were adsorbed on silica gel and the characteristic fluorescence was observed. In an attempt to show what groups are responsible for fluorescence, Bertrand (*5*) records the fluorescent spectra of many organic compounds and shows the effect of substituent groups. Forster (*35*) has made a similar study in an effort to determine the effective group in fluorescing dyestuffs.

The analysis of oils (*81*, *111*) and oil in water emulsions (*2*) may be accomplished by fluorometric analyses. In the latter case blotting paper is used to absorb the oil and this is compared to a standard under ultraviolet light.

BIOLOGICAL CHEMISTRY APPLICATIONS

Fluorometric analysis has found more application in biochemistry than in any other field. This has been especially true in the analytical chemistry of the vitamins. All modern texts dealing with the analysis of biological compounds give the fluorometric methods for riboflavin and thiamine and the subject is authoritatively treated by the Association of Vitamin Chemists, Inc. (*77*). Only a few of the very recent additions to this literature are mentioned here.

Kodieck (*60*), in an article on the fluorescence of vitamins and related compounds, discusses and gives references for the determination of thiamine, riboflavin, pyridoxal, nicotinamide, *N*-methylnicotinamide, cozymase, folic acid, and vitamin A.

Much work is of necessity in continuous progress on the determination of riboflavin in various materials—for example in general biological materials (*106*), in urine (*80*), in eggs (*75*), and in beef (*48*). Proper enzyme treatment of the material to be analyzed is necessary for the complete riboflavin assay (*95*). The quenching effect of electrolytes and the effect of hydrogen ion concentration are also factors which must be considered in the analysis of vitamins (*28*). Koff and Frederick (*61*) have shown that silicone lubricants serve as a nonfluorescing stopcock grease for these determinations. Johnson (*53*) and others have developed a rapid field test for the estimation of riboflavin, thiamine, and N^1-methylnicotinamide in urine. Over 100 specimens are run in a day.

The fluorometric determination of thiamine has been found, by comparison to biological and chemical methods, to be sensitive, reliable, and rapid. Brown (*14*) and others show a comparison of six different procedures for this assay. Williams and Wokes (*122*) have compared the fluorometric assay given in U.S.P. XIII for vitamin B_1 to other methods. It has been shown that factors such as temperature (*17*), the presence of reduced iron (*24*, *96*), and the proper hydrolytic enzyme (*16*) must be considered in the thiochrome determination of thiamine.

Brocklesby and Rogers (*10*) have been successful in the fluorometric titration of vitamin A with maleic acid in a benzene solution; and Sobotka (*108*) has developed a fluorometric method for the analysis of vitamin A esters.

Huff and Perlzweig (*50*, *51*) have devised a rapid and sensitive method for determining N^1-methylnicotinamide in urine by applying the condensation reaction with acetone and measuring the blue fluorescence. These authors and their co-workers (*70*) have extended the method to determine the total pyridine nucleotides in red blood cells.

Folic acid has been successfully determined by Villela (*114*) by using a measurement of fluorescence.

A fluorometric determination of ascorbic acid is described by Leupin and Steiner, (*69*) in which an ammoniacal solution of ascorbic acid is titrated with iodine. The intense blue fluorescence diminishes and at the end point changes to dark violet.

Lactoflavin responds to a fluorometric method, the details of which are given by Samaniego and Salgado (*97*).

A series of articles on the estimation of basic organic compounds in biological materials (*11–13*) shows the application of fluorescence in these determinations and has stimulated interest in the use of fluorescence in the determination of antimalarial drugs. The fluorescent spectra of some of these compounds of the chloroquine type have been measured by Price (*86*) and his co-workers.

Atabrine concentrations in biological materials are frequently determined by fluorometric methods. Auerbach and Eckert (*1*) have successfully determined 0.1 microgram in body tissue.

The fluorescence of adrenaline in sodium hydroxide solutions varies linearly with the concentration and thus provides the basis of a quantitative method (*54*). The fluorescence is apple green and a pH of 11 is most satisfactory.

Considerable progress has been made on the fluorometric determination of acridine derivatives. Vitolo (*115*) has compiled tables showing the reaction of a number of these.

Rutin (*40*) on hydrolysis with dilute acids yields quercetin, which is highly fluorescent and affords a convenient method for its determination.

A rapid fluorometric method has been suggested for penicillin by Scudi and Jelinek (*101*). The penicillin is condensed with 2-methoxy-6-chloro-9-(2-aminoethyl) aminoacridine and the method is applicable to concentrations of 0.0625 to 0.625 microgram of penicillin per ml.

The fluorescent method for determining chlorophyll has been known for some time. Kramer and Smith (*67*) have applied this to the determination of the ripeness of canned peaches and apricots; and Goodwin (*41*) has determined accurately less than 2 micrograms of chlorophyll a, using the mercury line 4047 Å. for irradiation.

The determination of coumarin (*105*) in sweet clover is relatively simple by the fluorometric method.

Tauber (*110*) has discovered what appears to be a specific fluorescent test for tryptophan which is not given by other amino acids and biological substances with which it is usually associated. The test depends on the formation of a yellowish-green fluorescent compound in the reaction of perchloric acid and tryptophan at room temperatures. It has also been shown that tyrosine, phenylalanine, and tryptophan will give a striking blue fluorescence when treated with Denigès reagent (*19*).

The determination by fluorescent measurements of certain carcinogenic and related hydrocarbons is discussed by Miller-and Baumann (*78, 79*), and Bergol'ts and Kofman (*4*). Fluorometric methods have been applied successfully to the analysis of pterins (*104*), sulfapyrazine (*93*), tocopherols (*62*), follicular hormones (*74*), carotenoids, and lipide amine-aldehyde products (*6, 27*).

Research workers in specific fields can undoubtedly add greatly to the fluorometric methods which have been outlined here. The wide diversity of applications indicates a considerable growth in popularity of this mode of analysis. The references given here are not exhaustive, but have been chosen to provide a starting point in the literature research on a particular topic.

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INSTRUMENTATION

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TO MINIMIZE duplication, this discussion is restricted to some general principles of instrument technology and the description of a few techniques and devices that are useful in analytical instrumentation.

The application of instruments to the solution of specific problems has been extensive and impressive. In a number of fields such as emission spectroscopy, infrared, x-rays, and polarography the references run to the thousands. Each new application confirms our belief in the value of instrumental methods but perhaps obscures the fact that there is, or should be, a distinct subject known as analytical instrumentation. In the author's opinion, this subject is concerned with a study of all known physical phenomena for their possible analytical use. It draws upon all known physical and engineering techniques in an effort to devise new instruments and analytical methods. It is often contended that the analytical problem is of paramount importance and that the means whereby it is solved is of secondary importance. The economic justification for this attitude is obvious, but problems, like the poor, are always with us and another solved problem just reduces by one the number awaiting solution. A new instrumental technique may permit the solution of a hundred new problems.

With the exception of industrial control instruments and some phases of engineering, instrument design is in the hands of gifted amateurs recruited from various branches of science and technology. It is truly remarkable how much has been accomplished in this profession for which there is, per se, no formal training. The theoretical basis for instrument design is in a highly developed state and although the tools and techniques are numerous, their full resources have been applied to a negligible degree.

Analytical instrumentation may be said to be developing in four general directions.

1. In the experimental stage are such techniques as microwave absorption, supersonics, nuclear activation, and neutron absorption.
2. The classical methods of spectroscopy, electroanalysis, and physicochemical methods in general are being refined and improved with emphasis on greater speed, precision, and automatic operation.
3. Feeble and second-order effects are being made amenable to measurement by rugged recording instruments. An excellent example is the recording Raman spectrograph. At the time of its discovery, and until only recently, the Raman effect required extended exposures and involved all the sources of error inherent in photographic photometry. These outweighed any specific advantages over other analytical methods. With the advent of the recording instrument an important scientific phenomenon has become a routine analytical tool.
4. Some attention is being directed to conductometric, refractometric, and thermal methods but relatively little compared with activity in the other categories. Most of these await new instrumental approaches for their more widespread use. In this respect, conductometric titrations afford a good example. Although widely quoted in all elementary texts, the technique remains a research tool and will not be used extensively in analysis until the time-consuming details are eliminated.

ELECTRONICS

One subject which has contributed heavily to modern analytical instrumentation is electronics. The modern approach utilizes the full resources of electronic circuitry as an intermediate stage in the over-all process of measurement. The earliest applications used vacuum tubes as primary measuring elements, but their instability and lack of reproducibility were constant sources of annoyance. Modern practice emphasizes the circuit in which a tube is used and, as far as possible, makes the performance of that circuit independent of tube characteristics. However, great progress has been made in improving tube performance. Developments in this respect are continuous and unremitting. The electrometer tubes and miniature tubes represent striking advances, but even the tube manufacturer will not advise one to rely upon tube performance when so much more dependability can be achieved through good circuit design. He is concerned with long life, reasonable uniformity, low cost, and trouble-free operation.

As an example of the many special-purpose tubes which are constantly being developed, Figure 1 shows a phototube specifically designed for facsimile service.

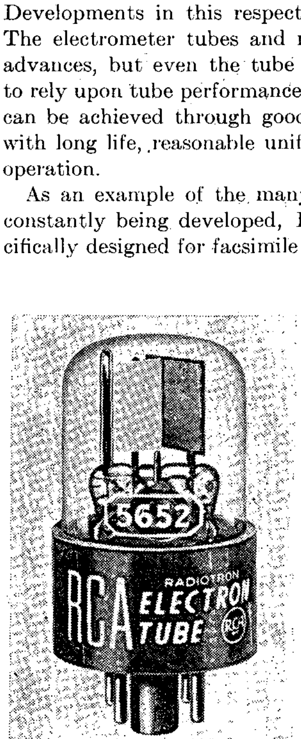


Figure 1. Electron Tube

There are three principal methods whereby electronics can serve without excessive dependence upon tube characteristics: (1) inverse feedback or degenerative amplifiers, (2) trigger circuits, and (3) servomechanisms employing electronic circuits.

Inverse Feedback. The first of these is a fundamental principle which dominates a good part of modern amplifier theory and practice. If a signal is fed to a high gain amplifier and a definite fraction of the output is returned to the input in opposition or out of phase, the partial cancella-

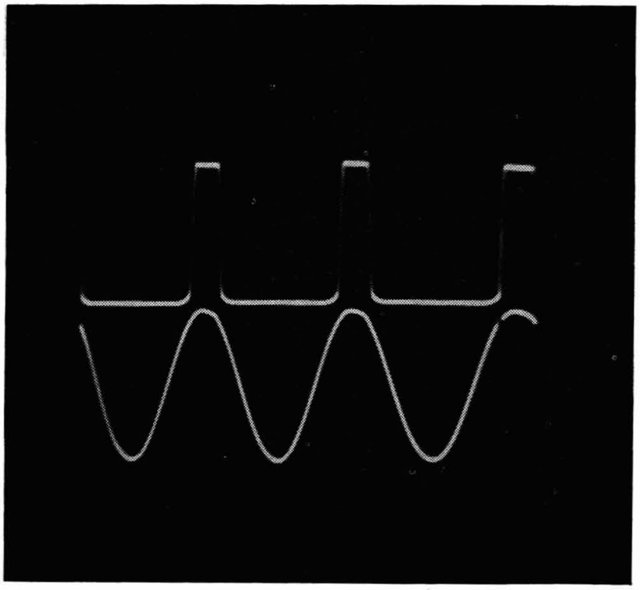


Figure 2. Oscillogram of Schmitt Trigger Action

tion will reduce the over-all gain but will greatly improve performance. It can be shown that as the degree of feedback approaches unity, tube characteristics and supply voltages have little or no effect on the residual gain. It might be inferred that in order to be effective, this process would have to be carried out until no useful amplification resulted. Actually a high order of stability can be attained, for example, by using an amplifier gain of 10^6 and degeneration to the extent of 10^4. This will leave an effective gain, with feedback, of 100-fold. An extreme form of this principle, employing complete feedback, is the cathode follower circuit. In this circuit the gain is always less than unity, but it retains several advantages, primarily as an impedance-changing device. Inverse feedback has been treated in countless papers and the theory and practice are described in most textbooks of electronics and communications as well as in an excellent monograph by Bode (*2*).

Trigger Circuits. Trigger circuits provide another approach to measurement and control which promise to revolutionize many fields other than nuclear physics, radar, and the other techniques in which they are already indispensable. They represent another instance in which an electronic circuit can be made to depend more upon simple circuit components such as resistors and capacitors than on tube characteristics. Trigger circuits are based on the principle of relaxation oscillators. Such oscillators are characterized by two stable states of equilibrium, with a highly unstable intermediate state. In a typical example, a twin triode may be so connected that the output of each section controls the input of the other. If one section is conducting, the other will be cut off. If an appropriate signal is applied to the nonconducting section it will begin to pass current and simultaneously start to cut off the other section. In a matter of microseconds, the initial state of the system will be reversed—i.e., the tube that was conducting will be completely cut off and its quiescent neighbor will now be conducting.

In the freely running multivibrator the switching from one state to another occurs continuously and automatically at a rate determined by the circuit parameters. In the so-called "one-shot multivibrator," one of the sections is biased to cut off by the output of the other and the system will remain in this state indefinitely. If a suitable triggering pulse is applied to the system, it will switch abruptly to the condition in which the conducting tube is extinguished and the other is turned on. After a finite interval the system will automatically switch back to the original quiescent state. The duration of the pulse can be varied over wide limits. This simple device can, among other things, be used to lengthen pulses—for example, if a brief transient, such as a momentary flash of light, were to be recorded, its effect could be prolonged sufficiently to permit a sluggish relay to close and record the event.

Another version, in which either of the two states is indefinitely stable, is known as the Schmitt trigger (*10*). The system can be triggered by making the grid of the first tube more positive with respect to its cathode. If it is now made somewhat less positive it will switch back to the original condition. The dead zone can be made as small as 0.1 volt and obviously much smaller by preliminary amplification of the signal. This circuit is unusually valuable in a number of chemical applications (*7, 11*). The rapidity of switching is shown in Figure 2. This oscillogram is doubly pertinent because the two patterns were presented alternately on the 'scope by an electron switch.

The lower portion of Figure 2 is a 600-cycle signal which was impressed on the input of a Schmitt trigger. The rectangular pulses in the upper part of the illustration show that when the sine wave signal attained a definite potential, the circuit triggered and caused the output potential to rise. The latter remained constant, as shown by the flat top of the rectangular pulse, until the sine wave potential decreased to a point where the circuit triggered back to its original condition. In this illustration, rapid sine wave excitation of the trigger circuit was used for the convenience of illustrating the rapid switching process. Actually this particular trigger circuit owes its distinction to the fact that it can be made to trigger with small changes in direct current potential.

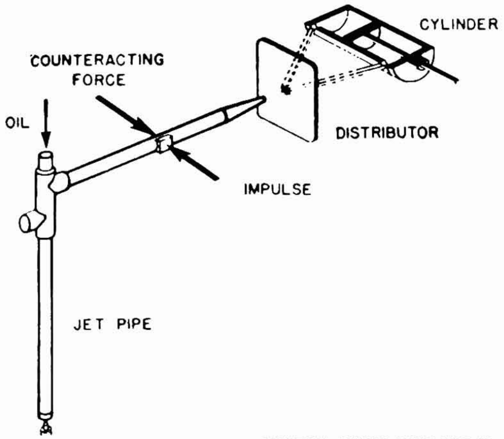
Trigger circuits may be considered as fast-acting switches, and for control or measuring purposes their principal advantage arises from the great difference in current which exists in either section when it is in the conducting or nonconducting condition. Under these circumstances, such matters as the critical pull-up and drop-out values of a relay become unimportant. Trigger circuits alone, or in combination, can perform countless functions: counting, scaling, pulse sharpening, lengthening or delay, time delay, frequency measurement and division, amplitude selection or discrimination, square wave generation, and production of time markers. In the last of these, it is simple to use these circuits to generate marker pulses representing definite time intervals and, by the addition of a few other triggers, to make every fifth pulse twice as large and every tenth pulse four or more times as large. Such markers may be presented on a cathode ray tube or may be placed directly on the phenomenon being traced on the tube in the form of blanking or intensifying marks. In this way a pattern will be broken up into dots or spaces, each representing definite time intervals.

A common application of trigger circuits is represented by the electron switch, by means of which two phenomena may be presented in rapid alternation on the screen of a cathode ray tube (as in Figure 2). In this application, two interrelated phenomena are fed to separate amplifiers, the outputs of which are presented on the 'scope. These amplifiers are switched on and off by the electron switch, so that the individual phenomena are presented alternately. Provision is also made for superimposing two pictures or, if desired, either one may be placed above the other. If the phenomena are temporarily related, either one or the other may be used to effect synchronization and lock them into position on the screen. Three or more phenomena may be presented simultaneously by cascading $n-1$ electron switches, although the advent of multiple-gun oscillographs offers a simpler solution. The literature on trigger circuits is very extensive (*3–5, 9*).

Servomechanisms. Servomechanisms involving electronic components are replacing the older methods of measurement and control (*6*). According to Hazen, a servomechanism is defined as a power amplifying device in which the amplifying element driving the output is activated by the difference between the input and the output.

The similarity between servomechanisms and inverse feedback will be recognized; indeed, the theory underlying each of these principles is identical. The most familiar example of a servomechanism is the modern recording potentiometer.

The small direct current potential to be measured is applied in rapid alternation to the primary of a transformer either by a rotating commutator or by a vibrating-reed converter. The alternating potential is fed to a high gain amplifier and then to a power stage. The output of the latter excites one winding of a two-phase motor, the other winding of which is excited in quadrature from the alternating current line. A shaft rotation results, the direction of which depends upon the polarity of the input signal, and its speed upon the magnitude of the signal. This shaft drives a recording pen, but what is more important and characteristic of the servo principle is that it also drives a slide wire which introduces a compensating potential in series with the unknown potential. It will continue to do so until the input signal is cancelled. Under these conditions, the electronic system is driving the motor and its associated components at all times at a rate which is proportional to the difference between the indicated potential and the true potential. The driving force will be zero when the two are identical. As the electronic system operates only on an "error signal," little demand is made upon its constancy. If the amplifier gain is excessively low, an appreciable dead-zone will result; if it is excessively high, the system will exhibit jitter or "nervousness."



COURTESY, ASKANIA-REGULATOR CO.

Figure 3. Askania Jet-Pipe Principle

The principle may be extended to almost any class of measurement or control, whether the system involves currents, potentials, radiant energy, fluids, or mechanical motions. It stands in marked contrast to our conventional laboratory habit of trying to fix every variable by means of thermostats, constant voltage transformers, shock-mounted supports, etc., and then hoping that everything will remain constant long enough to permit measurement. It does resemble the classical principle of a null method or intercomparison technique, but the difference lies in the use of a mechanism to effect this intercomparison automatically and at high speed.

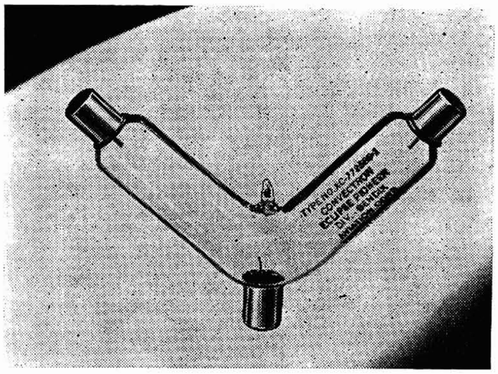
There are many variations of the servo principle and the final actuating means may be electrical, pneumatic, or hydraulic. Figure 3 illustrates the Askania jet-pipe principle of control in which a jet of oil is discharged against a pair of holes in a distributor block. These holes or orifices are connected to a cylinder on either side of a piston contained therein. The piston shaft acts as a thrustor element and can exert a very great force. If the output motion is returned to the jet-pipe deflector system in a restoring sense, the servo principle is attained and in consequence the load will follow very small and feeble forces exerted upon the jet-pipe system. Pneumatic control systems follow the same principles; in general, there is no fundamental difference as far as the choice of fluid is concerned.

The General Electric Autopot is a self-balancing potentiometer in which the unknown e.m.f. is applied to a mirror galvanometer. Light reflected from the mirror of the latter illuminates a phototube, thus upsetting the balance of a vacuum tube bridge circuit. Considered thus far, we would have a highly sensitive photoelectric amplification of a galvanometer deflection. This instrument, however, utilizes the important step of returning the bridge unbalance potential to the input circuit in opposition to the unknown e.m.f. The feedback in this case returns the galvanometer "almost" exactly to its original or zero position. The bridge unbalance current is therefore directly proportional to the input potential and heavy enough to operate a rugged meter or recorder. A more recent version of this principle substitutes a rugged deflection system for the galvanometer and a duplicate feedback coil affording electrical isolation from the input. It is sufficiently robust for use in aircraft.

A study of the present trends in electronics shows that the emphasis is on function and a greater utilization of the versatility of electronic circuits. As far as possible no dependence upon tube characteristics or reproducibility is sought. The electronic approach to a problem is to use more rather than less tubes for a given problem, especially if it can be shown that the additional tubes furnish compensation, regulation, and greater reliability. The chemist often attempts to reduce all operations to a single tube and frequently winds up with the necessity of water-cooling it to prevent overloading. More and more of our analytical instruments turn out to be a combination of three elements—the primary element or sensing device, an electronic system, and an output or power device which does the hard work of indicating recording or controlling. The added precaution of using a portion of this rugged output to effect input compensation or cancellation achieves the above described servo principle and thus puts the electronic portion of the system in its proper category—i.e., as the "brains" of the system.

PRIMARY ELEMENTS

Primary elements have the general meaning in instrumentation of any device that will convert a phenomenon into some form of energy which is readily magnified to a degree where it can be measured or made to actuate rugged mechanisms. A complete résumé of such elements would require several volumes, but it may suffice to describe a few special devices that illustrate the incessant search for more and better elements. Thermopiles, bolometers, and resistance thermometers are all ancient devices, yet the search for their improvement or for superior substitutes is as intense as the development in electronics. We seek better primary elements for the detection of radiant energy, nuclear particles, and dimensional or positional displacements; for the measurement of mass length, time velocity, and acceleration. There is no longer any excuse for dismissing any one of these on the basis that our present means are satisfactory, because it happens frequently that the improved technique is valuable in an entirely different application. Thus a method which may improve the measurement of linear displacement a hundredfold may solve a problem in radiometry. The modern investigator in this field is always aware of the resources of electronics and therefore does not ignore small or second-order effects.



COURTESY, BENDIX AVIATION CORP., ECLIPSE-PIONEER DIVISION

Figure 4. Y-Type Convectron

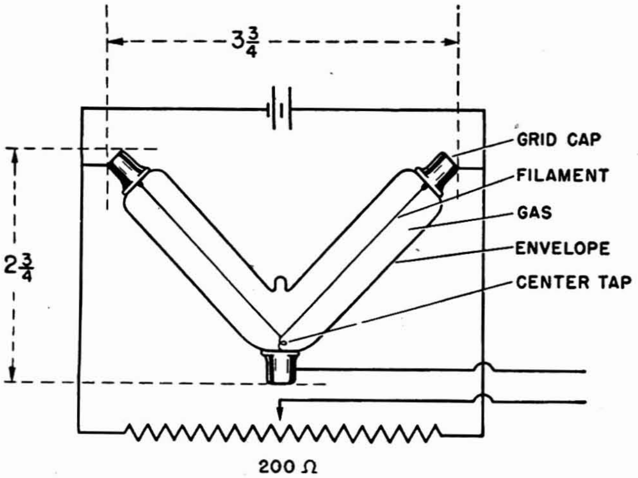


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Figure 5. Y-Type Convectron in Bridge Circuit

An interesting and useful example of a recent device is the Bendix Y-type position convectron shown in Figure 4. It is the electrical equivalent of the plumb line and liquid level for indicating the vertical or horizontal, respectively. The simple devices are inferior to the convectron as elements for automatic control because they oscillate before they settle in their stable position; because they have moving parts, their center of gravity shifts relative to their mounting, and finally they provide no simple means for obtaining a suitable electrical signal for control purposes. The convectron is a nonemissive tube capable of giving an appreciable electrical signal relative to its position about vertical. It consists of a sealed glass bulb with grid caps mounted at the end of each arm and at the base of the tube. The envelope is filled with argon and contains a single nickel filament running centrally through each arm to a spring support in the base which serves as a center tap for the filament.

COURTESY, BENDIX AVIATION CORP.

Figure 6. Chronotron Tube

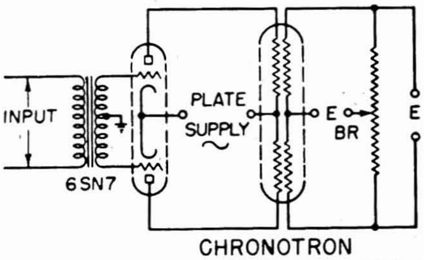

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Figure 7. Chronotron Tube Circuit

When operated in a bridge circuit as shown in Figure 5, the filament is heated to about 400° C. The design of the convectron is such that heat loss from the filament is primarily by convection rather than by metallic conduction, gas conduction, or radiation. The gas convection currents rise along the vertical and so pass the filament at whatever angle it happens to be relative to the vertical. Tilting the tube will cause unequal heat losses from the two legs of the filament and therefore unbalance the bridge. If the latter is operated from a direct current source, the output signal will reverse polarity at null. On alternating current the signal will reverse phase. In either case a servomechanism can be controlled by the device because the signal has directional discrimination—i.e., it knows whether the displacement has been to the right or to the left.

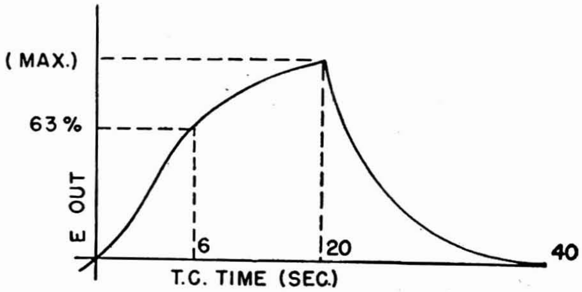
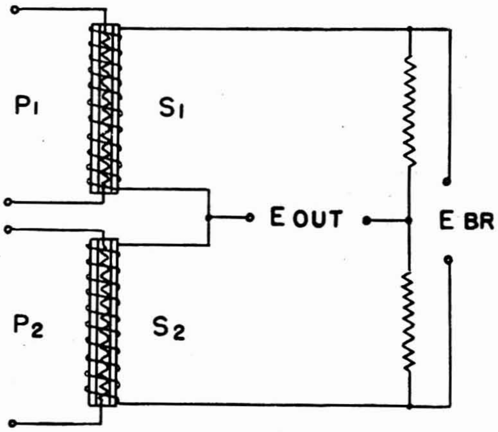


Figure 8. Voltage Increase and Decrease with Heating and Cooling

Using circuit of Figure 9

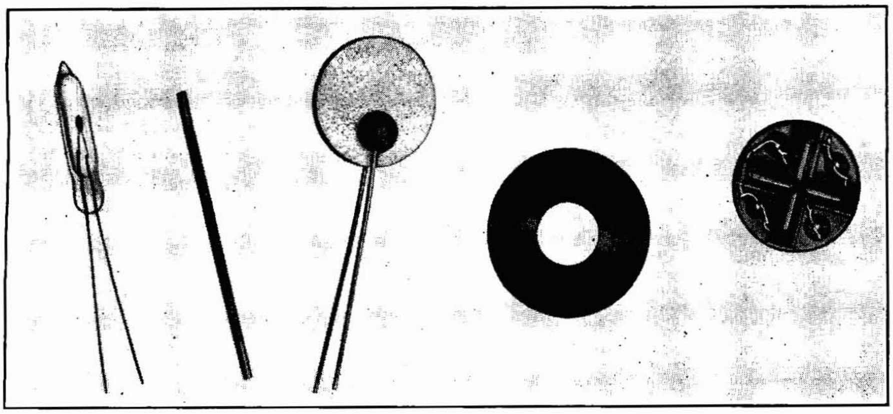
The time constant of the tube is about 0.1 second and the electrical signal is free of oscillations. The displacement signal is about 50 mv. per degree. For the measurement of extremely small displacements, direct current is used because there is no voltage at null. Displacements as small as 1 second of arc (less than one millionth of a revolution) can be measured, but at this sensitivity ambient temperature and bridge voltage constancy become important factors.

The Chronotron tube, also developed by Bendix, is a temperature-resistance device mounted in a miniature-size vacuum tube envelope (Figures 6 to 9). It provides time delay and also functions in a manner similar to an integrating device. The tube has two heaters and two secondaries. The secondaries are resistance windings used in a balanced bridge circuit. Any change in one heater current changes the temperature of the corresponding secondary and therefore its resistance and unbalances the bridge. The desired time constant is built into the tube by interposing an insulator of proper heat capacity between heater and secondary. If a signal is applied to one of the heaters, the output signal rises slowly and finally reaches a constant value. If this heater is cut off and the other is energized, the



COURTESY, BENDIX AVIATION CORP.

Figure 9. Typical Chronotron Circuit



COURTESY, WESTERN ELECTRIC CO.

Figure 10. Thermistors

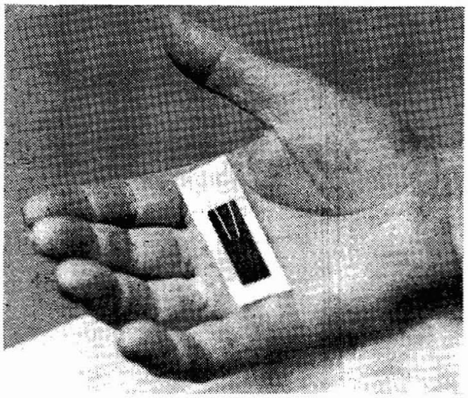


Figure 11. Strain Gage

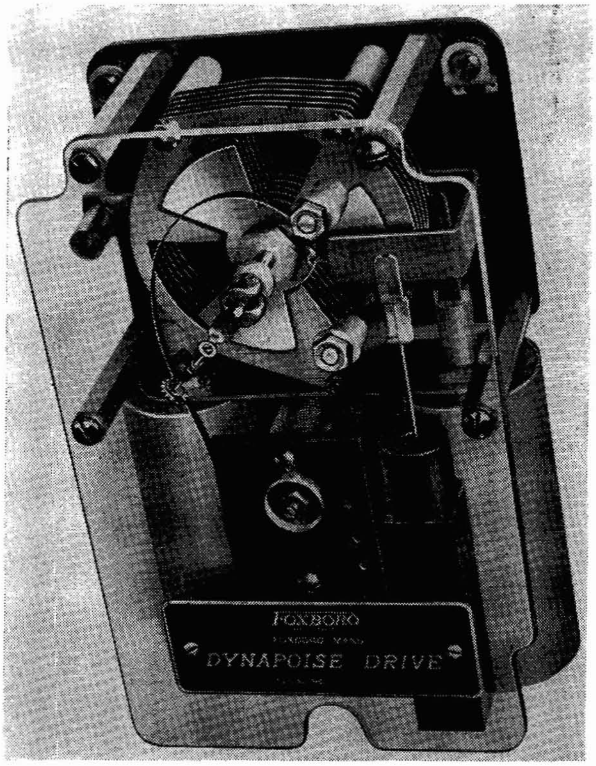
bridge output will decrease and rise again in opposite phase. The device is used primarily in the feedback loop of error-responsive servos to provide rate of correction signals, especially where high-inertia loads are involved. Either heaters or secondaries can be operated by direct or alternating current and in the latter case by any wave form.

Another primary element which promises to have very great influence on instrument design is the Thermistor, a circuit element in which electrical resistance varies widely with changes in temperature. It is made of a class of materials known as semiconductors. The negative temperature coefficient of resistance is unusually large; and this property, combined with unusual nonohmic characteristics, provides very unusual circuit possibilities. Thermistors are available in disk, rod, and bead types. A very comprehensive treatment of the properties of Thermistors is available in a recent paper by Becker, Green, and Pearson of the Bell Telephone Laboratories (*1*). Aside from their use in temperature measurement and control, Thermistors can be used indirectly for the measurement of high vacua gas or liquid flow, power measurement—notably in the microwave region—temperature compensation, and time delay, and as automatic volume regulators in electronics circuits. Some representative Thermistors are shown in Figure 10. These tiny elements have other useful properties, some of which are still in the experimental stage. For example, the negative resistance characteristic would indicate that in appropriate circuits they can be made to oscillate. This is one other example of the possibility that this and related devices may challenge the electronic tube in the performance of its varied functions. Indeed, the transistor very closely approximates the behavior of an amplifier tube, although its characteristics are different.

Strain gages have found very extensive use in engineering studies in the torsions and stresses produced in structural members, but since their capabilities have become more widely known they are finding more extensive use in other research laboratories. A *typical example*, shown in Figure 11, consists of fine wire bent in the shape of a re-entrant loop, embedded in a matrix which can be pasted or cemented to a surface in which an elongation or compression is to be produced. Their action depends upon an elongation of one part of the loop and a compression of the other part. Either motion will change the effective cross section of the wire and therefore its electrical resistance. These gages are very cheap, and often more than 1000 of them have been installed for a given test. They cannot be re-used, however, because the element is destroyed if an attempt is made to remove it. Strain gages will respond at very high frequencies, indeed, as high as 100 kilocycles. A number of these elements are readily incorporated in various bridge circuits or networks, so that components in several directions can be measured or recorded simultaneously. Obviously, numerous vector solutions are directly possible.

RECORDERS AND CONTROLLERS

There is an increasing trend in measurements of all sorts, and including analytical instrumentation, to record data automatically. This will become increasingly desirable, because (1) it relieves the tedium of recording individual measurements and the attendant possibilities of error, (2) it provides a permanent record of the measurement, and (3) more frequently than not, an automatic record will reveal small changes that might have been missed in manual point-by-point measurement. In the field of industrial measurements, recorders have held their undisputed place for a long time. In the field of scientific and laboratory measurements special requirements have arisen for which commercially available instruments require some modification. The



COURTESY, FOXBORO CO.

Figure 12. Foxboro Dynapoise Drive

chief need for improvement has been a matter of speed of response; and the newer recorders such as the Brown Electronik and the Leeds & Northrup Speed-o-Max G have answered this need. Despite the success of these approaches, there is an insistent urge to improve recorders in general. It may be useful to describe briefly a few methods that are not so well known.

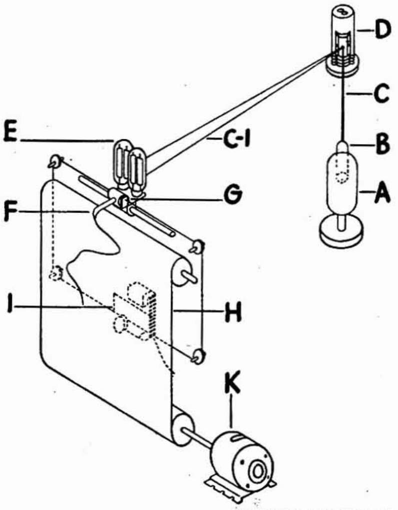
Figure 12 shows the Foxboro Dynapoise drive. In its use as a resistance thermometer, the resistance element is part of the measuring circuit which is supplied with 1000-cycle alternating voltage from a vacuum tube. The unbalance voltage is amplified by a factor of 10^5, and after detection the output of a power stage is directed to a coil in the Dynapoise drive. This coil, which is a solenoid, pulls on an armature and rotates a capacitor which rebalances the measuring circuit. The recording pen is linked directly to the balancing capacitor. The motion of the armature in the drive coil is accompanied by an opposite motion of another armature in an adjacent and identical coil, providing a feedback compensation in the output bridge. Advantages of this method over competitive techniques are the elimination of a slide wire with its moving contacts, and the need for a rotating motor with its accompanying reducing gears. The same instrument is applicable to e.m.f. measurements and, obviously, with the appropriate primary elements, to other phenomena or conditions such as humidity, pressure, flow, r.p.m., pH, etc.

Figure 13 shows the Photopen recorder manufactured by Beckman. The principle of this instrument was described by Pompeo and Penther (*8*). This recorder will follow rapid changes in the deflection of a beam of light as, for example, for a galvanometer mirror, by the simple expedient of having a twin phototube "chase" the light beam. As the schematic diagram shows, the phototubes are mounted on the pen carriage, and if either one of them receives more light, the reversible motor, *I*, will move the entire assembly in the appropriate direction to restore equilibrium. This type of recorder is obviously applicable to any class of measurement in which a beam of light is deflected, and naturally includes recording of all electrical phenomena which could be applied to a galvanometer.

There are numerous measurements which occur too rapidly for the best pen-and-ink recorder and yet too slowly for convenient presentation on a cathode ray oscillograph. This class of measurement is readily accommodated by the Brush magnetic oscillograph, shown in Figure 14. This will produce pen-and-ink records on electrical signals in the frequency range from direct current to 120 cycles per second. A very thorough discussion of the design of the magnetic pen motor for this instrument has been published (*11*). The frequency response is essentially flat, from 0.5 to 100 cycles per second. A striking example of its reliability is shown by the very creditable square wave which it will reproduce at a repetition rate of 100 cycles per second.

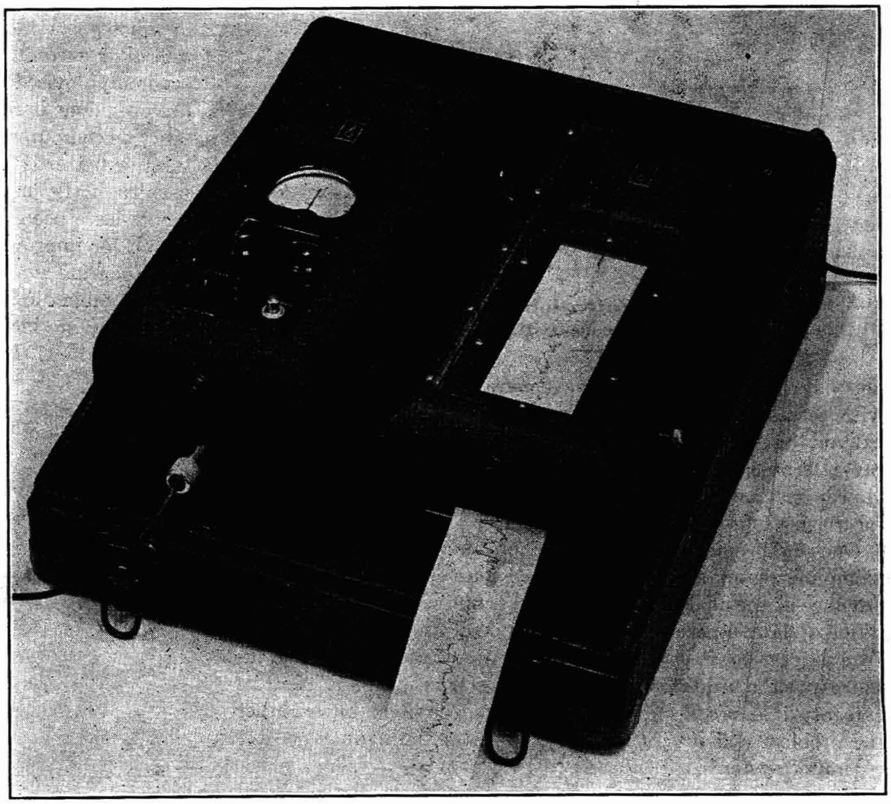
An intermediate case which presents difficulties in recording can be handled by the Brush transient recorder (Figure 15), designed to record and graphically represent varied transient phenomena of 0.2 second or less. In this instrument, the phenomenon is recorded magnetically on a rapidly moving steel tape by frequency modulating a carrier. After the phenomenon has thus been recorded, the tape is "played back" at a much higher but constant speed. A pick-up unit then presents the phenomenon on a cathode ray tube. The play-back feature is therefore a convenient means for speeding up the presentation to a rate at which it is conveniently viewed on an oscillograph. In common with other magnetic recorders, the tape record is readily erased by pressing a button, whereupon it is ready for a new record. The device is eminently suitable for recording vibrations, explosion waves, light flashes, and indirectly to any electrical, optical, or mechanical phenomena which can be converted to an appropriate electrical signal.

It is apparent to anyone familiar with the rapid developments in analytical instruments that the greatest emphasis is placed on means for measuring and recording phenomena of all classes with speed and precision. The resources of electronics and recording devices are such that one can expect to utilize almost



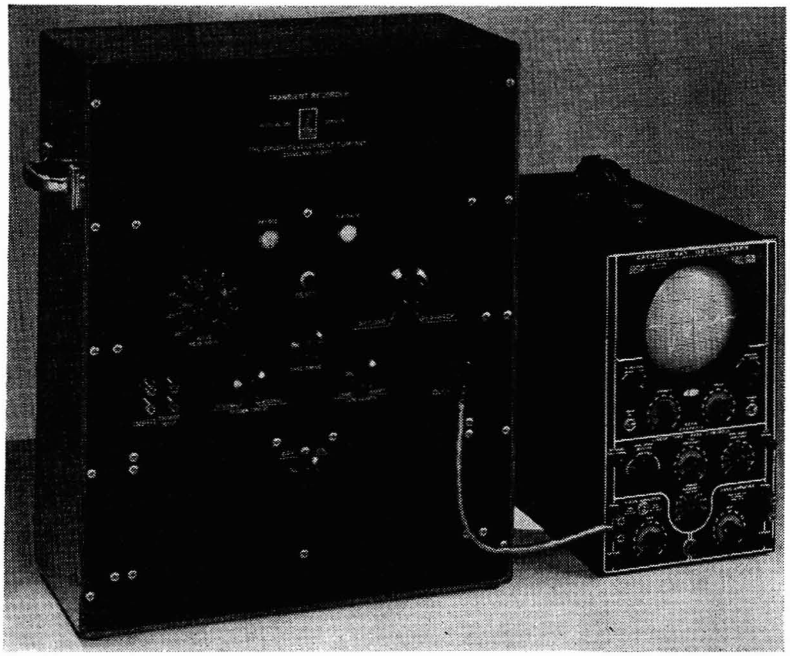
COURTESY, BECKMAN CO.

Figure 13. **Photopen Recorder**



COURTESY, BRUSH DEVELOPMENT CO.

Figure 14. **Magnetic Oscillograph**



COURTESY, BRUSH DEVELOPMENT CO.

Figure 15. Transient Recorder and Cathode-Ray Oscillograph

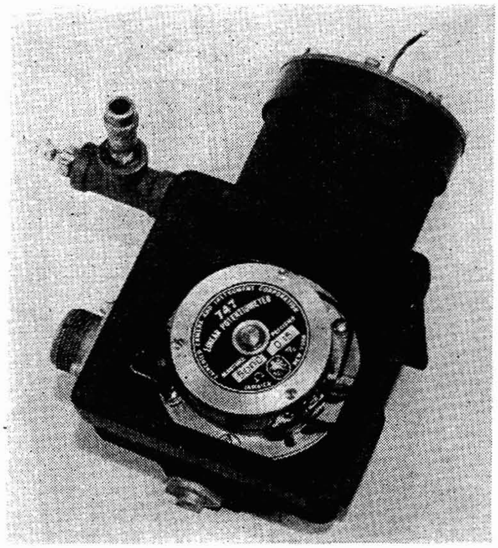


Figure 17. Potentiometer Applied to Pressure-Sensing Device

any natural phenomenon, however obscure or feeble, and know with certainty that it can be measured and recorded. To the extent that it can afford analytically useful information, it presents possibilities which the analyst cannot afford to ignore. He can rest assured at this stage that ample means are available for the measurement.

One final point is the matter of automatic computation. Computer theory and practice are in a state of development far in advance of the analyst's requirements; but with a rapid accumulation of data, especially in such fields as infrared, x-ray, and electron diffraction, it is becoming almost imperative for him to inquire into the utility of these techniques for his purpose. In this category it is not a question of what can be done, but whether the problem will justify the use of some of the more expensive computer systems.

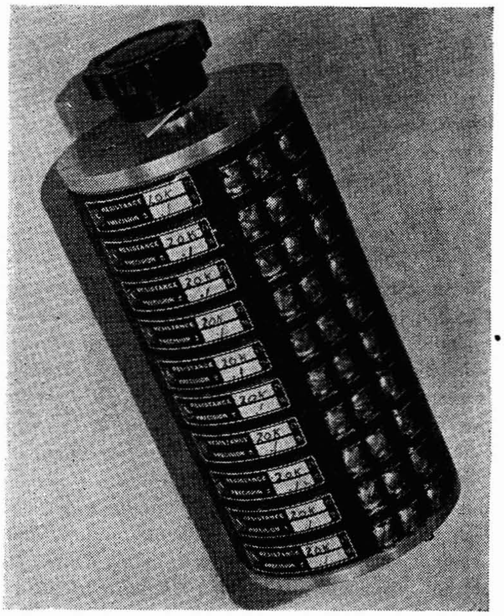


Figure 16. Linear Potentiometer

Most of the large computing installations are of the digital type and a greater degree of certainty and reliability results from the use of the binary system. It seems likely that the majority of the simpler computer requirements of the analyst will be met by analog computers of one sort or another. These can be mechanical, electrical, or electronic, or combinations thereof. It is a matter of common knowledge that mechanical devices consisting of levers, cams, gears, etc., can be combined to reproduce the simpler mathematical functions. The more elementary arrangements are subject to severe range limitations and often yield approximations to the desired function which are sufficient for the purpose. If more elaborate design is warranted and the best resources of modern machine practice are utilized, very precise results can be obtained. Much progress has been made in this direction (*12*).

Various electrical devices form the basis of computer networks in which the analog is furnished by an equivalent resistance, potential or current. Although rheostats and potentiometers were originally devised primarily for control purposes, much research has been done in recent years to increase their precision and reliability as computer components. Precision of one part in a thousand or better is a readily obtainable goal and life-expectancy is usually of the order of one million operations. These achievements have been the result of design research and the constant search for improved materials of construction. Special nonlinear tapers are available and these may be used singly (Figure 18) or in combination with a common shaft drive (Figure 16). Very often they are incorporated directly in a measuring primary element (Figure 17) from which they deliver a direct electrical signal

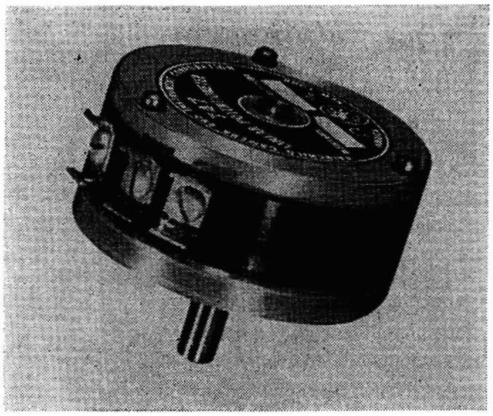


Figure 18. Single Potentiometer

or some simple mathematical function thereof. Selsyns, rotatable transformers, and related devices are important electrical computer elements. The versatility of electromechanical devices such as stepping relays or rotary switches is likely to be overlooked unless we recall their data-assimilating ability in the modern dial telephone system. Very useful computers can be assembled from electrical components. They may be adjusted manually to arrive at a numerical answer. Automatic adjustment may be arranged for, in which case the attainment of a solution results in a "zero" error signal and the automatic adjusting mechanism comes to rest.

Electronic circuits have inherent computing possibilities notably in counting. Other possibilities include addition, subtraction, multiplication and division, exponential functions, and differentiation and integration. A high degree of precision is rarely attained if one depends upon electron tube characteristics; but circuits can be designed in which dependence upon tube characteristics is minimized.

In taking full advantage of the best features of each class of computing element, it is not surprising to find that the more elaborate computers employed in navigation, gun laying, etc., usually employ all three methods, wherein a few simple mechanical elements are to be found which provide high precision electrical components, because of their versatility and flexibility and electronic components for their high sensitivity and almost complete lack of inertia. The net result is again a servomechanism which, because it is required to do very little heavy work, is designated as a computer-servo.

There is, perhaps, some irony in the situation; although some of the benefits and advantages of instrumental methods of analysis are still being questioned, there is ample evidence that in some measurements, data can be accumulated more rapidly than they can be assimilated.

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STATISTICS APPLIED TO ANALYSIS

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ANALYTICAL chemists have always used simple statistics such as the mean (arithmetic average) and mean deviation (arithmetic average of deviations from their mean) to summarize their test results (*10*). In recent years, they have begun to use some of the statistical methods that were developed by research workers in the fields of agriculture, biology, and medicine. It is the aim of this review to present a bibliography which includes references that explain these methods and show how they are being applied or can be applied in the field of chemical analysis.

The references to the statistical literature are not exhaustive. They have been included for the benefit of those who are not already acquainted with statistical methods. An effort has been made to include all papers in the chemical literature which deal with the use of statistical methods in analysis. It is possible that some important papers have been overlooked simply because the present abstracting systems do not make it easy to find papers which are reporting the results of statistically designed experimental work. Some references have been included which show applications of statistical methods in other fields in a manner which might be adapted for use in the field of analysis.

HISTORICAL

The famous statistician "Student" was one of the first to use modern statistical methods to study the results of routine chemical analyses. He showed (*108*) that the results of duplicate analyses are often correlated; and he pointed out that when this is so, the variability of duplicate analyses is by no means a true estimate of the variability of the method. He gave an interesting discussion of how important economically it is to distinguish between the precision and the accuracy of an analytical method. He also discussed the problem of discordant analyses and proposed a system somewhat similar to a control chart to help decide when such analyses should be rejected.

The first paper to appear in ANALYTICAL CHEMISTRY which made use of modern statistical methods was by Power (*90*). He presented the results of a carefully designed collaborative study of the precision and accuracy of the microanalytical determination of carbon and hydrogen.

In 1943, Moran (*83*) proposed a method of comparing the precision of a routine method of analysis with the precision of the method when used under the best conditions. This idea created a great deal of interest among analysts, and numerous papers have appeared since which have followed his procedure exactly. Briefly, it consisted in making ten analyses of a standard sample of material under carefully controlled conditions and calculating "limits of uncertainty" under best conditions. The same sample was then submitted to the routine laboratory at regular intervals, and limits of uncertainty under routine conditions were calculated. Moran found (as had "Student") that the routine analyses did not agree as well as might be predicted from the variability of results obtained under best conditions. Moran tried to establish some empirical relationships between the variability of the two kinds of analyses, but not very consistent ratios were obtained. Actually, it does not seem likely that any very close relationships really exist.

Moran suggested the use of the c_2 factor from the A.S.T.M. Manual on Presentation of Data (*2*, p. 50) to correct each group standard deviation for the constant bias which was introduced because it was calculated from a small number of individual determinations. This procedure is not recommended because the fluctuations of any statistic calculated from a small number of individual determinations are so great that the application of any factor to correct for a bias is an overrefinement. The c_2 factor does correct for such bias when a number of small group standard deviations have been averaged to give a more stable estimate of the small group standard deviation.

STATISTICAL QUALITY CONTROL

Perhaps the greatest single stimulus to the use of statistical methods in analysis was the series of short courses on statistical quality control which were sponsored by the War Production Board during the war. As a result of these courses, many chemists began to use simple statistical methods and to recommend the methods enthusiastically to others (*1, 11–14, 33, 36, 43, 50, 60, 69, 70, 72, 75, 76, 78, 79, 80, 81, 92, 93, 103, 105–107, 109, 111, 116, 118, 119, 120*). Most of these papers did not go into statistical theory or even into the details of how statistical calculations are made, but they did show numerous applications of statistical methods in a manner that analysts could readily understand.

THEORY OF STATISTICS AND STATISTICAL METHODS

It is very desirable that analysts become acquainted with the simple theory upon which statistical methods are based if they are to use these methods intelligently. A good elementary reference book such as that of Kenney (*67*) or Yule and Kendall (*134*) is indispensable. It is not safe to depend entirely upon any of the books on statistics which have been written by chemists or physicists.

A somewhat more advanced book, such as that of Hoel (*62*), will help answer many of the questions which come up with regard to the mathematical theory of statistics. The now classic book by Shewhart (*98*) will also throw light on many aspects of the theory and application of statistical methods.

Deming and Birge (*34*) have discussed at length the statistical theory of errors from the point of view of the experimenter. Bacon (*7*) has given a lucid explanation of a few of the important concepts and laws of statistics with a minimum amount of mathematical derivations. The interested analyst will find numerous references in those just cited which will direct him to the literature of the more theoretical aspects of statistical methods. The book by Yule and Kendall (*134*) gives a comprehensive bibliography on almost all phases of the theory of statistics.

FREQUENCY DISTRIBUTIONS

One of the basic statistical concepts is the frequency distribution; it is discussed in almost all books on statistics (*2, 51, 52, 62, 67, 98, 104, 134*). A few analysts have used frequency distributions to study and present experimental results.

Craig, Satterthwaite, and Wallace (*29*) made a study of the frequency errors in timing with electric clocks and presented their results in the form of histograms from which they made estimates of the maximum range found and the probable error of a single time measurement.

Hersh, Fenske, Matson, Koch, Mooser, and Braun (*61*) examined the optical rotations of 10% fractions for 372 different Pennsylvania oils and showed a histogram for the distribution of these values. They calculated the arithmetic mean, the standard deviation, and the skewness of the distribution and, by assuming a normal distribution, they estimated the number of oils that might be expected to have less than certain arbitrary optical rotation values.

Blyakher (*16*) studied the distribution of differences found between a new method for determining phosphorus pentoxide and a method which was well established. He fitted a normal distribution curve equation to his results and showed by means of a chi-square test of significance that the observed differences between duplicate analyses by the two methods did follow the normal law.

A detailed study of some 250 frequency distributions involving about 50,000 chemical analyses was made by Clancy (*25*). The analyses were of different kinds, such as the determination of impurities present as traces or in large amounts, assays of both crude and pure substances, and measurements of characteristics by physical and chemical methods such as are ordinarily carried out in the control laboratories of chemical industry. He found that 10 to 15% of these distributions could be considered as normal; the remainder were significantly not normal. He concluded that great caution must be exercised in applying ordinary simple statistical methods to the data of chemical analyses.

Wood (*125*) has expressed the opinion that this danger is not great so long as attention is directed primarily to the means of a series of observations, for it is well known that the distribution of means of a series of samples drawn from a population will usually approach close to normality even if the population is widely different from normal.

A reasonable explanation for some of these nonnormal distributions would be that assignable causes of variation were affecting the results. When these causes are removed, the distributions should approach closer to the normal distribution.

The use of frequency distributions will probably never find very wide use in analysis for at least two reasons: (1) Their use requires comparatively large numbers of measurements made under closely controlled conditions, and (2) there are many simple statistical methods available which will preserve the order of the data being studied so that assignable causes of unwanted variability can be more easily revealed.

CONTROL CHARTS

The statistical control chart was designed by Shewhart (*98*) and applied first to manufacturing problems. Most textbooks on the theory of statistics make no mention of control charts, but Grant (*52*) gives a comprehensive explanation of this very simple and useful statistical technique. The A.S.T.M. Manual on Presentation of Data (*2*) and the ASA War Standards (*3*) present the basic principles of using control charts, and the table of factors for calculating control limits is indispensable to anyone making control chart calculations. Control charts are explained and discussed in several other books (*19, 32, 47, 62, 98, 100*).

Several important papers on the theory and use of control charts have been published. Grubbs (*56*) discussed the "difference control chart" with an example of its use. This type of chart should find application in cases where absolute measurements are difficult to make and, as a result, it is necessary to make measurements relative to a controlled standard sample.

Hammer (*58*) discussed methods of estimating control limits when it is not possible to collect experimental data in logical rational groups. This case often arises when routine analyses are made once each day or once each week on continuous or large-batch chemical manufacturing processes. His moving range method will find application in these cases.

Duncan (*37*) explained the correct procedure for setting control limits when the number of observations in the various rational subgroups of a set of data are not equal. This situation often arises in the analytical laboratory.

During the war, many questions were raised about the practical use of control charts, and these questions are often asked by analysts even today. Schrock (*96*) answered most of them in an effective manner.

Control charts have been applied to many situations in the analytical laboratory. MacColl (*75*) showed their use to help check the accuracy of making routine analyses. Charts were run of the analyses of a standard sample in a single laboratory as well as for differences between the results obtained in two different laboratories. The chart for differences was more sensitive for detecting trouble. There was a correlation between the results of these two control charts, and it was estimated that 25% of the variation in the interlaboratory checks could be attributed to one of the laboratories. The contribution of the second laboratory could be estimated by correlating its results for the analysis of the standard sample against the control chart for differences.

Knudsen and Randall (*71*) studied the problem of making assay determinations of penicillin and used control charts to present the results of their experiments.

Mitchell (*80*) gave a thorough discussion of the meaning of reliability, precision, and accuracy of analytical methods in terms of the control chart. He explained a detailed method of using control charts to establish the reliability of a test method and estimate its precision and accuracy. Details of the arithmetical calculations were given for several examples.

Olmstead, Campbell, and Romig (*87*) used control charts to help interpret the results of a collaborative study of atmospheric corrosion.

Rawlings and Wait (*91*) studied the factors which affect the reliability and precision of the spectrophotometric determination of vitamin A.

Walker and Olmstead (*115*) used control charts to present the results of their experimental work in developing a new test for the resistance of textile materials to abrasion. They showed that their proposed yarn abrasion test gave statistically controlled data; they pointed out the practical advantage of using control charts for determining the reproducibility of such tests as corrosion, Izod impact, tensile strength, and elongation.

Wernimont (*118*) discussed the meaning that can be put into control charts and gave eleven examples of their use in connection with analytical problems. He also showed that simple factorial experiments could be designed so that the results might be studied by means of control charts (*119*).

VARIANCE ANALYSIS

Analysts, in general, have followed the classical method of conducting experimental work to design or improve analytical methods. This consisted in studying the effects of changing one factor while holding constant all other conceivable factors which were thought to introduce variability to the results of the experiment. In recent years, largely through the work of Fisher (*46*), the factorial type of experimental design has developed. In this type of experimentation, the effects of changing several factors in all possible combinations are studied in a single integrated experiment.

There are several advantages of factorial experiments over the classical one-factor-at-a-time kind. Perhaps the most important is that the factorial method makes possible the estimation of "interaction" effects among the different factors which contribute variability. Such effects are not even detected when the classical method is used, and yet they are often found to be responsible for the behavior of unsatisfactory analytical methods.

Variance analysis is usually used to help evaluate the results of these factorial experiments. In the case of simple one-factor experiments, there is a close analogy between variance analysis and the control chart method. Craig (*28*) has given a simple nonmathematical explanation of this relationship. A slightly more rigorous, but entirely understandable, discussion of the relation between control charts and variance analysis has been given by Scheffé (*95*).

The mathematical theory of variance analysis has been given in many books (*62*, *67*) and in several journal articles (*7*, *26*, *76*). Two important papers discuss the assumptions that must be made when variance analysis is used. In the first, Eisenhart (*39*) pointed out that two distinct classes of problems can be solved by variance analysis: Class I, detection and estimation of fixed (constant) relations among the means of subsets of the universe of objects concerned; Class II, detection and estimation of components of (random) variation associated with a composite population. He explained graphically the algebra involved in making analysis of variance calculations. He listed, in order, the assumptions which must be made in each case and then discussed when it is appropriate to use each model.

The second paper, by Cochran (*27*), discussed what errors are made when the assumptions for the analysis of variance are not satisfied. In general, the factors that are liable to cause the most severe disturbances are extreme skewness, the presence of gross errors, anomalous behavior of certain treatments or parts of the experiment, marked departures from the additive relationship, and changes in the error variance, related either to the mean or to certain treatments or parts of the experiment.

The problem of estimating components of variance has been considered by Crump (*30*) and by Satterthwaite (*94*). Satterthwaite concluded that the most efficient estimate of variance available is often too complicated for practical use; he suggested a satisfactory approximation.

Anderson (*6*) has presented a solution to the important problem which arises whenever a few observations are lost during the course of a factorial experiment. He suggested that observations should be rejected only under extreme circumstances, when it is obvious that the treatment being studied is not responsible for the apparently anomalous results. Objective methods of correcting for missing data were presented along with examples of their use.

In practice, the hardest way to make the arithmetical calculations of a variance analysis is to follow the algebraic definitions that are involved. Several books serve to simplify the arithmetic (*19*, *32*, *47*, *104*). The books by Brownlee (*19*) and Snedecor (*104*) can be especially recommended to those who do not want to be confused by abstract algebraic terminology.

Harris and Jesperson (*59*) have used variance analysis to study the relative merits of three methods of measuring the swelling power of starch. They studied the effects of three factors: (1) kinds of starch, (2) concentrations of starch, and (3) temperature. They found significant interactions between these factors, but were able to devise a satisfactory method of evaluating the swelling power of starch which would work under practical conditions.

Sandomire (*93*) studied the results of a cooperative test of the tensile strength of three kinds of rubber material. The factors studied were source of rubber material, testing laboratory, and effect of drying the samples before making the test. She found that the results depended upon the place where they were tested. Important interactions were also found, and she used a graphic method to show their magnitude.

Volz and Gortner (*114*) used variance analysis to evaluate the results of a factorial experiment on the relative merits of several methods of determining the peroxide content of pork fat. They found significant interactions between the level of peroxide in the pork and different conditions of the test. They were able to design a suitable method of analysis for use under all conditions that might be met while the test was being used.

Weybrew, Matrone, and Baxley (*121*) published the results of a designed experiment on the spectrophotometric determination of serum calcium. Two types of spectrophotometers were used, and the results were compared with a volumetric permanganate method. The experiment was designed so that it was possible to estimate the components of variance for different steps in the method, and the authors were thus able to point out what parts of the procedure might best be studied further.

Reitz and Sillay (*92*) studied the behavior of four physical testing machines and examined their results with the help of analysis of variance. They varied the type of jaw in the machine and tested eight types of paper. They found that at first the machines did not give identical results and were able to show that this was because one of the jaws was defective.

Wernimont (*119*) explained several examples of the use of variance analysis to help interpret the results of experimental analytical work, and made some comparisons between the variance analysis and control chart methods of studying the data.

Several analysts have used variance analysis to help evaluate the results of their experiments, but have published only their conclusions (*17*, *18*, *22*, *31*, *48*, *53*, *55*, *64*, *74*, *85*, *86*, *99*, *112*, *113*).

STATISTICAL CORRELATION

Various forms of statistical correlation are finding use in analysis. Bruner (*20*) gave a simple explanation of several useful kinds of correlation, along with examples of how the arithmetical calculations are carried out. Goffman (*49*) presented a simple discussion of multiple correlation in which an example of the calculations was explained in detail.

The fundamental statistical theory of correlation has been explained in almost all reference books (*62, 67, 134*). Deming (*35*) and Ezekiel (*42*) gave extended treatment to all phases of correlation theory and its application to practical problems. Most of the books on the applications of statistical methods devote a section to correlation (*19, 32, 47, 98, 100, 104*). Winsor (*122*) discussed the meaning which can and should be put into correlation studies.

Schwarz and Fox (*97*) have shown how correlation can be applied to help study testing methods in cases where relative measurements or subjective ratings must be made in place of objective test measurements. They included several examples. Olmstead and Tukey (*88*) recently published a new test for the association of two continuous variables which has three notable properties: (1) special weight is given to extreme values of the variable, (2) the computations are very easy, and (3) the test does not depend upon any theoretical assumptions (it is nonparametric). They used data from a metallurgical problem to illustrate the method.

By far the most useful application of correlation to problems of analysis was suggested by Youden to help study both the precision and the accuracy of an analytical method (*23, 77, 117, 128*). The analytical results of a series of "controlled samples" were correlated against the known amounts of the material in each sample. A regression line was fitted to these data by the method of least squares, and the precision of the method was estimated from the fluctuation of individual results from this regression line. When a method is accurate, the slope of the line should be unity and the line should extrapolate through the origin within limits calculated from the precision of the method. Failure of a regression line to meet these criteria was suggested as evidence that the method is not entirely accurate, and some idea of why this is so could be obtained, depending upon whether the slope, the intercept, or both are not conforming.

No papers have appeared in which Youden's suggested method has been used, although papers are continually being published with data already collected in a fashion so that it can be easily applied.

OTHER STATISTICAL METHODS

It is possible to mention only a few of the other statistical techniques which have been suggested. Evans (*40*) has given a good explanation of how the *t*-test can be used and interpreted. Newton (*84*) and Egloff and Kuder (*38*) suggested some simplifications for making calculations in the statistical analysis of physical-chemical data. The latter author also showed how to use the *t*-test to compose curves which have been fitted to observed experimental measurements. A comparatively recent development is the statistical method of "sequential sampling" which is clearly explained by Barnard (*8*). The principle was first developed to reduce the amount of sampling in the inspection of small piece-parts, but has been modified for use in almost any kind of experimental work. The number of samples or measurements is not fixed; it is determined by the results themselves. After each sample or observation has been obtained, simple arithmetic or graphic calculations are made, and one of three possible courses of action is taken: (1) the material is rejected, (2) the material is accepted, or (3) additional samples or measurements are obtained. The important advantage of this method is that, in the long run, the average amount of work is always less than that required when a fixed number of samples or measurements are used, and the probability of making incorrect decisions is kept the same.

Churchman (*24*) showed how sequential analysis might be used to help decide between two possible empirical formulas for an organic compound. The standard deviation of the method of analysis must be known from previous experiments. After each determination, it was possible to make one of the three decisions; and the analyses were continued until one of the two possible formulas was established as being correct.

Another advantage of the method is the fact that it is possible to set up different levels of probability for making wrong decisions in the same procedure. Westman (*120*) gave an example of this in which sulfamic acid was being recrystallized for use as a primary standard. The sequential plan was set up so that the risk of rejecting a good lot was 0.2, while the risk of accepting a bad lot was much lower, 0.01. This meant that some good lots were subjected to unnecessary recrystallizations, but very few bad lots were ever accepted and used as a primary standard.

It is sometimes necessary to make simple transformations of the raw data before statistical methods are applied. Biological assays require this kind of treatment and the system of probits is used (*15, 44, 70, 125*). Wood (*123, 124*) has given a detailed explanation of the theory of such procedures.

SAMPLING

Analysts talk a great deal about the importance of taking samples (*5*). They have designed complicated procedures for sampling some kinds of heterogeneous materials such as coal or grain, but in the vast majority of cases, they know very little about the relationship between the results they find on these samples and the true but unknown values of the lots which the samples are supposed to represent.

Simon (*101*) has discussed the importance of knowing the relation of samples to the lots from which they have been taken. He pointed out that wrong inferences are often drawn because of failure to understand what constitutes a lot and to verify the existence of a lot in the practically useful sense. Statistical methods are beginning to be used to help study sampling problems (*15*).

Beaudry (*9*) has suggested a method of studying the efficiency of commercial blending machines, and his method might be adapted to the study of samples for analysis.

Kenney (*66*) made a most thorough study of the methods of sampling raw sugar, and was able to simplify the procedure without decreasing its reliability. Lowry and Junge (*73*) reported the results of an extended study of sampling coal and coke. Youden and Mehlich (*133*) used a statistical approach to the problem of taking samples of soil. Villars (*112*) made a statistical evaluation of the variability of sampling plantation latex. Woods (*126*) gave a statistical treatment to the problem of sampling heterogeneous material. He showed examples of how to determine objectively the proper size of sample to take in order that the probable error of the final result would be less than any arbitrary value.

Youden and Mehlich (*133*) used a statistical approach to the problem of taking samples of soil. Youden (*129*) studied the variability of sampling and analyzing apples for their arsenic content. He concluded that the sampling variabilities were almost certainly greater than the variabilities of analysis.

Analysts need to become more interested in studying the variability of their sampling methods because, as Tukey (*110*) observed, it is absurd to strive for improvements in analytical methods when these methods are applied to samples with a much greater inherent variability.

Wallace (*116*) published a method of estimating the relative magnitude of sampling and making routine chemical analyses. He pointed out that the discrepancy between the true analysis of a batch and the results obtained in the laboratory is due to three main factors: (1) sampling errors, due to nonhomogeneity of the batch or contamination (which includes changes on standing, such as evaporation) of samples; (2) analytical errors due to the nonreproducibility of the analytical method as measured by the difference between two analyses in parallel of the same sample by the same analyst; and (3) analytical errors due to changes in technique by different analysts, or by the same analyst on different occasions. A fourth factor, due to a relatively constant difference between the result of analysis and the true composition of the sample, is normally corrected for, if necessary, by performing a standardization on a sample of known composition. Wallace gave an example of how to estimate the magnitude of these factors, using control chart methods.

DESIGN OF EXPERIMENTS

The importance of the design of an experiment becomes very apparent when statistical methods are used to help analyze the results. If an experiment is not correctly designed, it will often be impossible to give a rigorous answer to the question that gave rise to the experiment. Illustrations of this state of affairs can be found in almost any issue of ANALYTICAL CHEMISTRY.

Recently the results of an intercomparison of ten Beckman spectrophotometers was published in which it was concluded that the variability of absorption measurements from the various instruments was greater than the variability of measurements made on the same instrument (*41*). The authors stated that this was "presumably due to slight differences of manufacture in a sensitive instrument of this type." Actually, when statistical methods are used to study their data, it is impossible to substantiate this presumption because the variabilities of analysts, absorption cells, and test solutions have not been separated from the variability of the instruments. It would have been possible to design the original experiment so that, with about the same number of total observations, the effects of these anticipated sources of variability would have been separated and measured.

The design of experiments has long been a part of agricultural and biological experimentation, largely because of the work of Fisher (*45*, *46*). Most books on the use of statistical methods devote a section to this topic (*19*, *32*, *47*, *51*, *104*). Several papers discuss the general problem of the design of experimental work (*12*, *54*, *59*, *63*, *89*, *93*, *102*, *103*, *123*, *128*, *130*, *131*).

Goulden (*51*, Chapter V) gives a good explanation of how the design of an experiment affects the variability of the error term in the analysis of variance. The interpretations which can be made from a carefully designed experiment are explained in many papers previously cited under analysis of variance (*18*, *59*, *64*, *72*, *85*, *92*, *93*, *114*, *118*, *121*, *127*, *128*, *130*, *131*, *132*).

Grubbs (*57*) has shown that, by the proper design of experiments, it is possible to separate and evaluate the precision of a control method of analysis while using it to test production lots of material.

Hotelling (*65*), Kishen (*68*), and Mood (*82*) have suggested experimental designs which will reduce the uncertainty of the final measurements, such as weighings without increasing the total amount of experimental work very much. Actually, the designs suggested could not be applied to gravimetric analyses, but they might be used in the case where a large number of analytical weights are to be compared with a single standard weight.

STATISTICS IN CONTRIBUTIONS TO THE LITERATURE

Numerous papers have already been published on the importance of using statistical methods in analysis; a few papers explain in some detail how to use them. We need more papers of the latter type, which explain a single statistical technique using examples from the field of analysis. Details of the methods of calculation should be given along with the interpretations that can be made from the results.

Not too many papers have yet begun to appear in which actual use has been made of modern statistical methods. It is safe to say that the quality of contributions to the literature of chemical analysis will improve as analysts make more use of these methods.

The question of how much statistical treatment should be included in a report of experimental work is very important. Anderson (*4*) has given a most satisfactory answer. He suggests that "the first step toward writing a good paper is to plan the investigation soundly, and in this work, a knowledge of statistics will often prove helpful. Routine statistical analysis of data may present many pitfalls, and the advice of a professional statistician is frequently required. In most technical papers, statistics should not play the leading role, but a supporting one. Feature and discuss the data, not the statistics. Leave the statistics out if this is permissible, or put them in a separate section. And if you must discuss them, avoid esoteric jargon and use plain English."

LITERATURE OF STATISTICS AND STATISTICAL METHODS

The literature on statistical methods and their applications is rather widely scattered. Butterbaugh (*21*) published an extensive bibliography on statistical quality control which included publications through 1945. Wood (*125*) reviewed the literature on the application of statistics to chemical analysis prior to 1947.

The Journal of the Statistical Association, published quarterly by the American Statistical Association, 1603 K St., N.W., Washington 6, D.C., lists the titles of most of the contributions to the current scientific literature which have discussed or made extensive use of statistical methods in the design of experiments or the interpretation of results. It often publishes new contributions to the literature on the application of statistical methods, many of which may find application in analysis.

The American Society for Quality Control, 220 East 40th St., New York, N.Y., publishes the monthly magazine *Industrial Quality Control*, which often features articles of interest to analysts.

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INORGANIC MICROCHEMISTRY

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MICROCHEMICAL analysis can be considered to include the sampling, separation, detection, and estimation of minute amounts of material, regardless of the techniques employed. Quite properly, emission spectroscopy, polarography, chromatography, and similar techniques, which are fields within themselves, fall under the broad classification of microchemistry. For the present paper, however, a limitation of scope is made to prevent overlapping with other reviews, and the reader is referred to such other reviews to complete the orientation on progress in the general field of microchemistry.

The review of inorganic microchemistry does not include, except for isolated cases, papers on light microscopy, electron microscopy, nucleonics, polarography, fluorescence, or electroanalysis. Emission, absorption, Raman, ultraviolet, infrared, x-ray, and mass spectrometry are also excluded, although there may be duplication with absorption spectrometry, because microanalysis is so closely allied with color systems and their evaluation.

Organic microanalysis is reviewed separately. In addition to carbon, hydrogen, and oxygen, nitrogen, sulfur, phosphorus, and halogens present as integral parts of organic molecules are left for review elsewhere.

On the basis of coverage, the present review logically should extend to the general microchemical reviews of Nadler (*281–286*), and an attempt has been made at least to list the pertinent articles appearing since those publications. Other significant reviews include those by Wyatt (*411*), Chandelle (*57*), Sanborn (*323*), and Reimers (*311*). Developments in quantitative methods were discussed by Grassner and Abrahamczik (*144*) and Sobel (*343*), while work in the field of submicromethods was discussed by Zurcher (*430*) and Wilson (*406*). Wyatt has reviewed the methods of microfiltration (*410*) while Ingram (*174*) has reviewed various microchemical techniques, and Belcher has critically reviewed reagents and methods available for the determination of potassium (*25*). Dithizone was also discussed by Beaumont in regard to its applications in both qualitative and quantitative analysis (*22*). The use of electrometric methods in microchemical analysis was reviewed by Ashcraft (*14*) and by Lindsey (*228*). Biochemical applications of general microchemistry were critically reviewed by Kirk (*186*), and Sozzi (*344*) has published a more recent review in this field. The history of microanalysis has been given by Hillis (*161*).

Educational aspects of microchemistry, the teaching of microchemistry, and the advantages and disadvantages of micromethods in educational laboratories are of continuing interest. A discussion of value along these lines is that of Cheronis (*58*) although not restricted to inorganic analysis, and the articles of Kuck (*203*) and Wilson (*407*) are of interest to teachers. Very thought-provoking discussions of the use of quantitative inorganic microanalysis in teaching are given by Miller (*263*) and by Gaddis and Breckenridge (*129*). The latter article describes very encouraging results obtained in the undergraduate course on introductory quantitative analysis when micro- and semimicromethods are employed; the ordinary analytical balance was used for all weighings, based on the method of Benedetti-Pichler (*36*). The article by Choppin, Le Rosen, and West describes one approach to fitting microanalysis into the basic chemistry curriculum (*65*).

Feigl has contributed greatly to the teaching of chemistry as well as to the application of microchemistry to practical analytical problems. In a series of articles in the *Journal of Chemical Education* (*99*) he has presented a carefully integrated selection of experiments using new approaches in technique and distinctively fresh topics for study. In addition, his "Manual of Spot Tests" (*100*) provides a good theoretical and practical background in that field and his "Specific and Special Reactions" (*101*) provides a most complete reference on the principles and applications of organic reagents, complex ions, catalyzed and induced reactions, and other topics of interest in microchemistry. Benedetti-Pichler (*32*) presents a fundamental course of study of inorganic microtechniques.

APPARATUS

The development of microchemistry is dependent on advances in instrument and apparatus design together with disclosures of new reagents, reactions, and techniques. Because there is much art as well as science involved, not all advances are capable of easy description. Apparatus, for example, can be appraised best by actual observation and test. The thorough study of microchemical balances by Rodden *et al.* (*317*) was most useful, however, and the treatment of sources of errors in balances, such as the Kuhlmann balance, by Corwin (*71*) is worthy of note. Martin (*252*) has discussed types of balances and sources of error. Balance designs are given by Nanjundayya and Ahmad (*288*) as well as by Stock and Fill (*350, 356*). The application of the ordinary analytical balance to microchemical work as discussed by Benedetti-Pichler and Paulson (*36*) has proved to be a valuable contribution, while the description by Kirk and co-workers of a stable torsion balance having a sensitivity of 0.005 microgram with a capacity up to 0.1 to 0.2 gram will certainly prove important (*187*).

Two important papers describing absorption cells for spectrophotometry should be noted. Lowry and Bessey (*236*) described a small quartz cell and pointed out certain of its applications, and Kirk, Rosenfels, and Hanahan (*188*) described a capillary absorption cell to be used with a Beckman spectrophotometer which extends the limits for absorptometric analysis to sample sizes in the order of a few millimicrograms. This represents a sensitivity range approximately a million times greater than is usually employed in microanalysis.

Apparatus and techniques of importance in titrimetric work have been considered by Allan (*10*), Holt and Stringer (*165*), Isakov (*176*), and Korotkov (*200*). Lacourt and Timmermans (*210*) proposed a useful calibration procedure for microburets based on a titrimetric standardization against delivered biiodate. An automatic buret which avoids indirect volume measurement has been described by Lacourt, Stoffyn, and Timmermans (*209*), and an automatic buret made from thermometer tubing was presented by Llacer and Sozzi (*233*). Loscalzo and Benedetti-Pichler (*235*) suggest the use of a microgram pipet connected to a leveling bulb for delivering volumes of titrants up to 0.05 cu. mm. The titrations can be applied to 0.05- to 0.5-cu. mm. samples with precisions of 8 to 15 parts per thousand. A discussion of various types of apparatus for microvolumetric work was published by Masters (*254*). Syringe-type burets have been proposed by Nordmann (*293*), by Shaffer, Farrington, and Niemann (*335*), and by Stock and Fill (*355*). Rieman (*314*) proposed a modification of Benedetti-Pichler's horizontal buret to permit titrations of alcoholic solutions.

Apparatus for extractions are discussed by Belcher and Randell (*28*) and by Stock and Fill (*351*). Bowden (*43*) proposed a special filter thimble for use in cylindrical funnels. An excellent review of various devices and techniques for microseparations was given by Burton (*51*). A simple microtorch was proposed by Dacus (*79*), and a mercury bath described by Hewitt (*160*) has possible applications in inorganic microchemistry. The electric heater designed by Cifonelli (*66*) should prove useful for drying precipitates. Devices for evaporating and drying include the evaporating "spoon" of Belcher (*26*) and Holt (*164*). The clever suggestion of Rulfs (*320*) relating to the use of baby bottle warmers as water baths for microchemical work is worthy of note (and is a thirfty idea for retired fathers). Stock and Fill have made suggestions for reagent bottles for microchemical applications (*352*), ground joints for small-bore tubing (*354*), and clamps for objects of small diameter (*353*). A wash bottle made from a specimen tube was suggested by Thomas (*364*), and an electrode control device for microchemical electrodeposition was proposed by Lindsey (*229*).

Apparatus for use in gas analysis include micromanometers described by Brow and Schwertz (*49*) and by Hindley (*162*), and a pressure regulator proposed by Furter and Steyermark (*128*). Nash (*289*) described a microeffusiometer that can be used to determine molecular weights on 0.5 mg. of volatile liquid with accuracies of better than 2%. A method for studying gas reactions at high pressure was presented by Leipunskiĭ and Reinov (*216*), and Grushevskiĭ (*151*) has designed a new apparatus for microanalysis of gases based on indirect measurement of gas volumes from estimation of expelled measuring liquid. The apparatus of Kenty and Reuter (*182*) employing freeze-out techniques is capable of determining carbon dioxide, hydrogen, carbon monoxide, and oxygen in minute samples with accuracies of better than 2%. Price and Woods (*306*) have described a method for analysis of microsamples of inorganic gases that can be applied for the detection and examination of bubbles in glass.

Various gadgets of use around the microchemical balance were listed by Wilson (*408*), and the general design of microchemical laboratories has been considered by Ingram (*173*) and Warth (*382*). The report of the Committee on Specifications for Microchemical Apparatus should be noted (*319*).

ORGANIC REAGENTS

Progress in inorganic microchemistry depends to a great extent on the development of new organic reagents. Many of the precipitants used in microchemical work are organic compounds, since favorable equivalent weight ratios can be obtained to increase sensitivities in various determinations. In addition, the possibility of influencing solubility, selectivity, and color characteristics of organic reagents adds to their potential value. The consideration of individual reagents will be left for brief comment under subsequent discussions of spot test analysis, colorimetric analysis, etc. A number of papers of general interest, however, require separate comment. Yoe and his co-workers continue to contribute significant reagents, and progress of their program of investigation of new organic reagents may be followed in the *Virginia Journal of Science* (*126*, *223*, *329*, *418*). Yoe and Sarver (*426*) have reviewed the uses of organic reagents, and Yoe has compiled a selected bibliography on the subject (*418*). Kul'berg has presented a thorough discussion of sensitivity and specificity as related to ionic radii and active groups (*205*), and has classified organic reagents on the basis of salt formation, complex formation, etc. Other reviews include those by Barcelo (*18*), Belcher and Spooner (*29*), Bulíř (*50*), Druce (*87*), Kuzentsov (*207*), Majumdar (*244*, *245*), Mesnard (*260*), Shome (*336*), Steigmann (*345*, *346*), and Voznesenskiĭ (*381*).

The combination of organic reagents with other techniques is of interest. Stone and Furman (*357*) have used 8-hydroxyquinoline as a precipitant for magnesium and determined the excess reagent polarographically without removing the precipitate. The method gave accurate results and was essentially free of interferences when the determination was performed in properly buffered solutions.

Feigl and Suter have contributed to the theory of inner-complex salt formation with a study of the salt-forming properties of various metal complexes of dimethylglyoxime (*116*); they were able to show that both of the oximino groups of dimethylglyoxime are capable of entering into complex formation by preparing barium, lead, and other salts of dimethylglyoxime–palladium acid, $H_2[Pd(C_4H_6O_2N_2)_2]$. West (*396*) has studied the nature of the reaction between *p*-acid fuchsin and palladous and gold salts and has concluded that the palladium-fuchsin reaction product has the form of a polynuclear or "network" complex. The possibility of chelates having large rings has been overlooked by analytical chemists up to this time, and confirmation of their existence would open new fields for investigation. The work of Ubeda and Gonzales (*372*) may be significant in this connection, and the earlier work of Spacu with the compounds formed between such salts as copper thiocyanate and benzidine can be explained on the basis of polynuclear complex formation.

MICROCHEMICAL SEPARATIONS

Many individual and group separations have been proposed, and Benedetti-Pichler and his students have contributed valuable studies on the adaptation of classical systematic separation schemes to microchemical uses. Cases of individual applications are generally inherent parts of the respective analytical procedures and so will not be considered separately. Group separations, however, merit special notice, and attention is directed to the articles by Benedetti-Pichler and Cefola (*34*, *35*) and Konig, Crowell, and Benedetti-Pichler (*196*).

A number of general techniques for microchemical separation have been described. Abrahamczik (*1*) has used isothermal diffusion to separate reagent chemicals from possible impurities, while Bayliss and Pickering (*20*), Lacourt and Chang (*208*), and Stock and Fill (*351*) have employed extraction methods for making analytical separations. Erbacher (*95*) has investigated the separation of unweighable quantities of material.

Chromatographic methods of separation have attracted major attention. Copper has been separated on an ion-exchange column prior to polarographic determination (*72*) and Lecoq (*215*) has made an interesting study of the possibilities of combining chromatography and electro-osmosis. As there is a separate review on chromatography, no discussion of other papers is called for. A number of excellent papers have dealt with inorganic microchromatography (*21*, *75*, *89*, *170–172*, *214*, *333*, *378*).

One of the most promising methods of separation, and certainly the most elegant, is complexation. Unfortunately, new complexing (masking) agents or new applications of established complexers are seldom designated in the titles of papers and so pass without notice by abstractors. The only way to find such agents then is to use trial and error methods or to develop the "art" through years of reading and observation. One or two references may be cited to show the possibilities of this method of separation but complete coverage of the subject seems impossible. West has found that malonic acid is an excellent masking agent for removing interferences in the spot test detection of copper using dithio-oxamide (*398*). Hale has employed citric or tartaric acid to prevent interference of molybdenum in the gravimetric determination of sodium with zinc uranyl acetate (*157*), and Popov has eliminated chromium, manganese, and iron interferences in the detection of vanadium by converting them to stable phosphate complexes (*305*).

GRAVIMETRIC ANALYSIS

Freri (*124*) has advocated the use of alcohol in certain precipitations to facilitate the mechanics of transferring and washing precipitates. A review of the reactions of 8-hydroxyquinoline

(*259*) is of value in gravimetric work. Tinsley (*368*) has made a comprehensive review of the use of cobaltinitrite for the microdetermination of potassium, and Ingram (*175*) has surveyed the use of combustion methods in metallurgical analysis.

Individual determinations proposed include the determination of alkaline earths by precipitation as the molybdates (*275*) as suggested by Moser and Robinson, and the determination of copper with anthranilic acid as described by Wenger and Besso (*388*). Mayr (*256*) proposed the use of gallic acid as a precipitant for lead and pointed out that bismuth would not interfere if it were first precipitated in dilute nitric acid solution; lead does not precipitate under those conditions and is subsequently brought down from sodium acetate solution. Important studies were made by Voter, Banks, and Diehl on the use of 1,2-cyclohexanedionedioxime for the detection and determination of nickel (*379*); these studies were extended to include the use of this reagent for the analysis of palladium (*380*). Kuras studied the use of diaminoglyoxime as a nickel reagent (*206*) but concluded that it was not so accurate as dimethylglyoxime for this purpose. Hale has studied the determination of sodium in the presence of molybdenum (*157*) and advocates citric or tartaric acid as a sequestering agent. Alimarin (*5*) has developed a gravimetric absorption method for the determination of water in minerals, ores, and rocks which employs a platinum catalyst, a mixture of lead oxide and lead dioxide as an adsorber for sulfur trioxide, and a silver spiral as a halide adsorber. The gravimetric determination of small amounts of vanadium can be accomplished by precipitation of silver vanadate, according to Kroupa (*202*).

TITRIMETRIC ANALYSIS

A wide range of methods and applications have been studied in the field of microchemical titrations. Stock has reviewed the subject of potentiometric methods (*348*) and three important articles have recently appeared. Stock has pointed out the applicability of dead-stop end-point methods in titrating very small volumes of liquid (*349*). The very interesting possibilities of the high frequency oscillator has been considered from the microchemical standpoint by Blake, who employed a 1175-kc. frequency radio-oscillator (*41*); and Meyers and Swift (*261*) have shown that the coulometric titration of arsenic is capable of yielding results accurate to 1 microgram.

A number of studies have been made on the determination of sulfur. Zimmerman has found that a fusion method using potassium serves to open up most substances. Acid is then added and the hydrogen sulfide formed is distilled over and titrated iodometrically (*429*). Alimarin and Sheskol'skaya (*9*) determined sulfate by adding an acidic solution of barium chromate and measuring the chromate liberated by adding standard ferrous sulfate and titrating the excess with standard ceric sulfate. Ogg, Willits, and Cooper (*296*) found that using an illuminated titration stand permits the easy identification of the tetrahydroxyquinone (THQ) end point in sulfate titrations. This has been confirmed by Steyermark, Bass, and Littman (*347*), who modified the procedure by employing a Carius combustion for preparing the sample for titration. The titrimetric determination of calcium has been studied by Kochakian and Fox (*193*) and by Dymov and Rozhkova (*91*).

Leithe has investigated the dichromate titration of nitrates and its application (*211, 218, 222*), the indirect titration of chlorides (*219*) and sulfates (*220*), and the acidimetric titration of phosphoric acid in fertilizers, foods, and soils (*221*). Kieselbach has also investigated the determination of nitrates and recommends the use of Devarda's alloy for reduction to ammonia followed by hydrochloric acid titration (*183*); a similar method is used for the determination of nitric oxide.

Chlorometry has been recommended for microchemical analysis by Goldstone and Jacobs (*138*), who point out that sodium hypochlorite solutions are very stable when properly prepared. The method can be applied for a number of determinations, including the titrations of arsenic and antimony.

Pollard (*303*) investigated means of detecting, separating, and determining iridium, and Lespagnol and Merville (*224*) proposed an iodometric method for the determination of gold. The titration of small amounts of fluorides using thorium nitrate was advocated by King and Luhorn (*185*). Alimarin (*7*) presented a method for the determination of iron in minerals; and Montequi and Doadrio (*273*) described a titrimetric procedure for molybdenum. Reith and Gerritsma investigated the determination of thallium in excreta and tissue and found that while larger amounts can be determined gravimetrically, amounts of thallium less than 0.1 mg. are best determined by iodometric titration (*312*).

Water in minerals has been determined on small samples by means of the Karl Fischer reagent (*321*). The determination of small amounts of chlorates has been studied by Williams (*402, 405*) and both an iodometric and a ferrous sulfate-dichromate procedure have been developed. The titrimetric carbonate determination advocated by Grangaud includes a diffusion process for absorbing carbon dioxide in barium hydroxide followed by acid titration of excess absorbent (*142*). Luke has developed a method for determining mercury in rubber based on a Volhard titration (*238*); he has also proposed methods for the determination of arsenic, antimony, and tin in lead alloys (*239*).

The iodometric determination of thionalide has been investigated by Lalic (*211*), who found that time affects the results. The use of thionalide as a precipitant with subsequent titration, for the indirect determinations of metals, should be restricted to microchemical work. Dithizone has been used as a titrant in the determination of mercury by Eckert (*92*), and Yao has used it for titrating traces of bismuth in copper (*415*).

SPOT TESTS

Spot tests provide an almost ideal method for qualitative analysis. There is always need for new reagents and new methods for "conditioning" test reactions and it is not surprising, therefore, that a very significant amount of work has been published over the period covered by this review. The application of spot test procedures in the investigation of tin-base alloys has been considered by Evans and Higgs (*97*), and Thrun and Bartelt (*367*) have listed various spot tests to be used in examining steels. Niessner (*291*) has dealt with the application of spot tests in general metallurgical work, and Claeys and Gillis have used semiquantitative spot tests for examining steels (*67*). Acosta (*2*) has presented a qualitative analysis scheme employing classical group separations of cations followed by appropriate spot test identifications.

Numerous tests for individual cations have been published. Feigl and da Silva have described a method for detecting basicity of slightly soluble substances (*113*). Feigl and Barbosa (*103*) described a new test for detecting acidity, and discussed the dipicrylamine test for potassium (*104*). Feigl and Suter (*115*) discussed the analytical uses of sodium rhodizonate. Feigl and Braile described the uses of sodium rhodizonate in various analyses (*107*), the detection of elementary sulfur and selenium (*108*), the detection of traces of lead in water and fine chemicals (*106*), and the spot test detection of lead (*105*); they also studied the application of spot tests to the identification of calcium sulfate (*109*). Another application of spot tests was given by Feigl and Dacorso who studied the detection of reducing substances (*110*); these authors have also reviewed the uses of the catalytic iodo-azide reaction (*111*) for the detection of insoluble sulfides. Feigl and Suter (*114*) have shown how small amounts of permanganate can be detected in the presence of large amounts of chromate. Feigl and Miranda (*112*) have used the α,α-bipyridine–ferrous complex for the spot test detection of cadmium; the test is both sensitive and selective. A test for silver has been proposed by Baker and Reedy (*16*) employing potassium iodide as reagent; a special procedure for eliminating interferences is given. Ashburn and Reedy (*13*) have published an excellent test for vanadium based on the use of sodium tungstate in acidic solution. A yellow color is obtained with as little as 4 micrograms of vanadium and there are no interferences, since phosphoric acid is used very effectively as a sequestering agent. Another spot test for vanadium is the benzidine-aniline (or naphthylamine) test of Popov (*305*) and here, also, phosphate complexes are formed as a means of eliminating interferences.

The detection of nickel in steel by means of a rapid spot test was described by Vance and Gonser (*375*). A modified Gutzeit procedure for the detection of arsenic was recommended by Catoggio (*55*), and Costenau (*72*) used the familiar ferrocyanide reaction for detecting and determining iron. Bismuth can be detected using glucose, according to Fonseca (*121*), although copper is a serious interference. A sodium fluoride bead test is given by Northup (*294*) and cobalt can be detected with sodium thiosulfate as the reagent (*310*). Goldschmidt and Dishon (*136*) utilize the copper bromide complex as a means for detecting copper.

Wenger and co-workers have made a number of fundamental studies on the relative merits of various tests. Wenger's extinction method for semiquantitative spot test analysis is also interesting (*394, 395*). This method requires the use of various tests of varied but known sensitivities; noting which tests fail and which ones are positive gives an indication of concentration.

Various spot tests for palladium have been suggested. Konig and Crowell have found that thioglycolic or thiomalic acids give yellow colors with as little as 0.05 microgram of palladium (*196*), and that phenoxathiin forms an addition complex with palladium and can be used as a sensitive reagent for this metal (*194*). West and Amis found that pararosaniline hydrochloride is a very sensitive reagent for palladium and devised a specific test based on its use (*399*). West and Tokos (*400*) suggested the use of brucine citrate for the detection of bismuth, and West developed a specific and sensitive test for copper using dithiooxamide with malonic acid as a conditioning agent (*398*). Feigl and West have provided a sensitive and specific test for selenium based on a catalytic reaction involving a selenosulfide complex (*117*).

A number of other catalytic tests have been proposed. Lang (*213*) has used the catalytic effect of molybdenum on the hydrazine–methylene blue reaction as the basis for detecting molybdenum, and Llacer has developed a test for mercury employing the catalytic acceleration of stannous chloride reduction of silver ion (*232*). Goto and co-workers have devised catalytic tests for iodine (*140*), sulfide, thiosulfate, and thiocyanate (*141*), and copper and silver (*139*). The sodium azide test for sulfur has been discussed by Hahn (*156*).

Gillis, Hoste, and Claeys have studied the uses of various fluorones. They found (*135*) that methylfluorone can be used to detect selectively 1 part of antimony in 2,500,000 and that germanium can be detected by means of phenylfluorone (*134*). The use of *o*-hydroxyphenylfluorone was recommended as a reagent for molybdenum and copper (*133*). Thio derivatives of salicylaldehyde were studied by Beck (*24*) and it was found that substituting —SH for —OH groups improves the usefulness of such reagents. Tests for various heavy metals are given.

Spot test patterns have been obtained by Yagoda (*414*) for studies of mineral and biological materials. Electrographic methods for detecting molybdenum have been given by Calamari, Hubata, and Roth (*53*) and by Vaes (*374*). Rust patterns on iron and steel have been tested by Clark (*68*) using potassium ferrocyanide.

A number of tests have been suggested for detecting various halides. Martin tests for fluorine by converting it to silicon tetrafluoride (*253*) and Llacer uses benzidine in testing for iodine (*231*). Llacer tests for bromine by a modified Denigès-Chelle test (*230*), as does Weiner (*385*). Fluroescein is employed by Hach and Franke (*155*) for detecting chlorides and bromides. A spot test for carbonate employing barium hydroxide has been presented by van Dalen and de Vries (*80*) and a sensitive, specific test for thiocyanate has been described by Mennucci (*258*).

Skalos has advocated the use of "acro tests" (*337*) as a means of increasing the sensitivity of various spot tests. He has also described a "one-drop method" of employing spot tests, which is claimed to give increased sensitivity (*338*).

COLORIMETRIC METHODS

The great majority of colorimetric determinations are microchemical methods as published, or can be easily adapted for spot test work, trace analysis, microcolorimetry, etc. Inasmuch as a separate review on colorimetry is included in the present survey, the discussion of this subject in the review of inorganic microchemistry is condensed as much as possible to prevent unnecessary duplication. A rather complete list of publications in the field of colorimetric analysis is included in the bibliography.

The work of Mellon and his associates on colorimetry and color systems is of great importance (*147, 189–191, 268, 276–279*). Cholak and Hubbard have made numerous studies in the field of colorimetric determination of metals in biological materials (*60–64*), including the determination of microgram quantities of cadmium, zinc, aluminum, lead, and mercury. The work of Sandell on trace analysis (*324, 326–328*) is of primary importance, and the studies of organic reagents and their colorimetric and spot test applications (*419–421, 423, 424, 426*), conducted by Yoe and his associates, are of great value.

Schleicher (*331*) has published an interesting commentary on how to select the best colorimetric procedures for adaptation to microchemistry. The excellent books on the subject of colorimetric and trace analysis should be noted. A table of various colorimetric determinations is included to provide a means of easy reference (Table I).

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[Table of colorimetric determinations and bibliography are found on pages 125 to 131]

Table I. Colorimetric Determinations

Element	Reference	Reagent or Method	Sensitivity
Aluminum	(*64*)	Alizarin Red S	0.01 to 0.10 mg./100 ml·
Ammonia	(*226*)	Nessler's reagent	
Antimony	(*23*)	Various	
	(*123*)	Rhodamine B	0 to 20 γ
	(*163*)	Iodide	0.35 to 1.5 mg./50 ml.
	(*249*)	Rhodamine B	0 to 40 γ
	(*240*)	Iodide	10 γ
Arsenic	(*137*)	Gutzeit method	1 γ
	(*178*)	Molybdenum blue	1 γ/ml.
	(*243*)	Molybdate	0 to 100 γ
	(*249*)	Molybdate	1 to 10 γ
	(*326*)	Molybdate + hydrazine	1 γ
	(*330*)	Gutzeit method	0.01 γ
	(*359*)	Molybdate + hydrazine	0 to 100 γ
	(*361*)		75 to 100 γ
Bismuth	(*166*)	Dithizone	0 to 10 γ
Boron	(*37*)	Turmeric	0.05 to 1.0 γ
	(*384*)	Quinalizarin	0.001 to 0.005%
	(*409*)	Turmeric	0.2 to 1.2 γ
Bromine	(*39*)	Brucine, strychnine, cinchonidine	0.01 to 0.05 milliequivalents
Cadmium	(*60*)	Di-β-naphthyl thiocarbazone	0 to 5.0 γ
Chlorine	(*39*)	Brucine and strychnine	0.01 to 0.05 milliequivalents
	(*362*)	Methyl orange	0.10 to 1.3 p.p.m.
Chlorate	(*405*)	*o*-Tolidine	5 p.p.m.
Chromium	(*40*)	*o*-Phenanthroline	11 γ
	(*93*)	*s*-Diphenylcarbazide	0 to 20 γ/11 ml.
	(*340*)	$Fe(ClO_4)_3$	0.007 to 1%.
Cobalt	(*52*)	NCS^-	
	(*74*)	*o*-Nitrosophenol	5 γ
	(*83*)	NCS^- and$(Fe(CN)_6)^{---}$	
	(*94*)	*o*-Nitrosocresol	0.02 to 25 γ
	(*277*)	Terripyridyl	0.5 to 50 p.p.m.
	(*297*)	*o*-Nitrosoresorcinol	0 to 2.5 mg.
	(*361*)	NCS^-	
	(*370*)	Nitroso R	0.01 mg.
	(*401*)	Nitroso R	20 γ
	(*427*)	NCS^-	0 to 0.5 mg.
	(*428*)	Nitroso R salt	0.01 to 0.5 mg.
Copper	(*30*)	Dithizone	0 to 12 γ
	(*70*)	Dithizone	0.1 p.p.m.
	(*76*)	Tetraethylenepentamine	1 to 200 p.p.m.
	(*274*)	Dithizone	0 to 6 p.p.m.
	(*278*)	1,10-Phenanthroline	0.5 to 10 p.p.m.
	(*295*)	Dithizone	
Cyanide	(*131*)	Prussian blue	0.2 γ
Fluorine	(*98*)		0.5 γ/drop
	(*177*)	Purpurin	20 to 60 γ
	(*212*)	Zirconium-alizarin	10 γ
	(*272*)	$TiCl_3$	30 to 160 γ/50 ml.
	(*360*)	Thorium-alizarin	0.1 p.p.m.
Germanium	(*189*)	Molybdate	0 to 30 p.p.m.
Gold	(*324*)	*p*-Diethylaminobenzylidenerhodanine	0.1 p.p.m.
Indium	(*269*)	8-Hydroxylquinoline	0.3 to 20 mg./l.
Iodine	(*39*)	Brucine, strychnine, and cinchonidine	0.01 to 0.05 milliequivalent
	(*88*)	Thiofluorescein	1.27 γ/10 ml.
Iron	(*3*)	NCS^-	0.4 to 7 γ
	(*8*)	Sulfosalicylic acid and NH_4OH	
	(*17*)	*o*-Phenanthroline	40 γ
	(*46*)	1,10-Phenanthroline and diethyldithiocarbamate	0 to 50 p.p.m.
	(*146*)	1,2-Dihydroxybenzene-3,5-disulfonate	0.025%
	(*147*)	Nitroso R salt	0.2 to 50 p.p.m.
	(*148*)	Dioximes	
	(*158*)	NCS^-	0.2 p.p.m.
	(*179*)	2-Nitroso-1-naphthol	2 γ/ml.
	(*227*)	Dimethylglyoxime	0 to 1 mg.
	(*302*)	1,10-Phenanthroline	0.5 to 1.0%
Iron (*Contd.*)	(*361*)	NCS^-	
	(*365*)	NCS^-	0 to 70 γ
	(*121*)	4-Hydroxybiphenyl-3-carboxylic acid	10 p.p.m.
	(*422*)	Disodium-1,2-dihydroxybenzene-3,5 disulfonate	1 part in 200,000,000
Lead	(*47*)	Dithizone	0.1 to 0.001 mg.
	(*62*)	Dithizone	0 to 100 γ
	(*332*)	Dithizone	0 to 550 p.p.m.
	(*342*)	Dithizone	1 to 450 γ
Magnesium	(*83*)	8-Hydroxyquinoline	0.39 to 1.5%
	(*159*)	Tropaolin	0.0001 mg.
	(*204*)	*p*-Phenylenediamine	6.4 γ/1.
Manganese	(*130*)	Persulfate	
	(*198*)	Oxine	15 γ
	(*403*)	KIO_4	0.37 p.p.m.
Mercury	(*61*)	Di-β-naphthylthiocarbazone	1 γ/100 ml.
	(*201*)	Dithizone	50 to 100 γ
Miscellaneous	(*276*)	8-Hydroxyquinoline	
Molybdenum	(*38*)	Dithiol (4-methyl-1,2-dimercaptobenzene)	0 to 50 γ
	(*181*)	NCS^-	0 to 5%
	.(*150*)	$CNS^- + SN^{++}$	0.01 to 630 mg.
	(*387*)	Toluene-3,4-dithiol	
	(*300*)	Potassium xanthate	0 to 10 γ
Nickel	(*268*)	Dimethylglyoxime	0.1 to 5 p.p.m.
	(*83*)	NCS^-	
	(*83*)	$Fe(CN)_6^{---}$	
	(*4*)	Diethyldithiocarbamate	5 to 80 γ
	(*154*)	Dimethylglyoxime	0.1 mg.
	(*244*)	Oxanilic acid thioamide	
	(*299*)	Dimethylglyoxime + pyridine	2 to 50 γ
	(*334*)	Dimethylglyoxime	0.1 to 1.0%
Nitrate	(*292*)	Brucine	0 to 50 p.p.m.
	(*153*)		0 to 9 γ
Osmium	(*327*)	Thiourea	3 to 10 p.p.m.
Phosphorus	(*45*)	Molybdate	0.002 to 0.4%
	(*191*)	Molybdate	2 to 10 p.p.m.
	(*190*)		1 to 40 p.p.m.
	(*271*)	Molybdenum blue	0.01 mg.
	(*304*)	Molybdenum blue	0.0 to 0.7 mg.
Platinum	(*12*)	Thiosemicarbazide	50 to 100 γ
Selenium	(*86*)	Phenylhydrazine	0.01 mg.
Silicate	(*262*)	Molybdate	
Silicon	(*44*)	Molybdenum blue	0.002 to 0.056
	(*369*)	Molybdate + C_2O_4	0.02 to 2.0 p.p.m.
Silver	(*248*)	Tannin	0.008 to 0.25 mg.
	(*339*)	Dimethylglyoxime	2 γ
	(*363*)	Dimethylaminobenzalrhodanine	1 γ
Sodium	(*11*)	Uranyl acetate + H_2O	0.2 to 2 mg.
Sulfur	(*361*)	Benzidine	
Sulfate	(*192*)	Benzidine	0.05 to 0.15 mg.
Sulfur dioxide	(*143*)	Fuchsin	0 to 10 γ
Tellurium	(*82*)	Hydrazine $SnCl_2$	5 to 140 γ
Tin	(*15*)	Silicomolybdate	0.0005 to 0.5%
Titanium	(*267*)	Hydrogen peroxide	0.001%
	(*419*)	Disodium-1,2-dihydroxybenzene-3,5-disulfonate	0.01 γ
Tungsten	(*149*)	$NCS^- + SnCl_2$	0.04 to 0.4 mg.
	(*328*)	$NCS^- + SnCl_2$	0.5 p.p.m.
	(*38*)	Dithiol (4-methyl-1,2-mercaptobenzene)	0 to 50 γ
Uranium	(*246*)	Quinalizarin	3.5 to 9.5 p.p.m.
	(*78*)	NCS^-	50 to 800 γ
Zinc	(*63*)	Di-β-naphthylthiocarbazone	0.0 to 50 γ
	(*48*)	Dithizone	0.005 to 0.01%
Zirconium	(*423*)	5-Chlorobromamine	10 p.p.m. min.
	(*145*)	Alizarin S	0.003 mg.

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Organic Microchemistry

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MICROCHEMICAL analyses of organic compounds still follow largely the pattern set by Fritz Pregl. Considerable strides have been made during the past 6 years, as evidenced by the increase in the number of microchemical laboratories and the wider application of microanalytical chemical techniques. During the late twenties and early thirties, microanalytical methods were but little used in the United States except in the Atlantic Coast states. Ten years later these methods had been introduced into the midwestern states, and today micromethods are in use in analytical laboratories throughout the country.

The keen interest shown in the development of microchemical analysis is exhibited by the establishment of a committee on the performance of microchemical balances (A. H. Corwin of Johns Hopkins University, chairman); a revival of the committee on standardization of microchemical apparatus (A. Steyermark, chairman); and the re-establishment of a referee on the standardization of microchemical methods by the Association of Official Agricultural Chemists. The British Standards Institute has formed a subcommittee to standardize microchemical apparatus, and the work of this subcommittee is well advanced. Microchemistry has gone a long way since Pregl devised this scheme of analysis, for it is no longer limited to the analysis of material available in only small amounts. Instead, it has an accepted place, along with micromethods, for the analysis of materials available in large amounts. The micromethod is superior, in that it is faster, more economical of reagents, and in many instances more precise and accurate.

In expanding micromethods, some analysts have used larger samples and others extremely small ones. The committee on apparatus is now in the process of analyzing the results of a questionnaire by which it hopes to determine the extent to which semimicroapparatus is used and how much adherence there is to the microequipment. Because of the expansion of micromethods to cover weights from a few hundredths of a microgram to 50 mg., they have been forced to prefix the term micro with such descriptions as "semi" and "ultra." These prefixes are not adequate, because each may cover so wide a range; thus semimicro may mean anything from 10 to 50 mg. Even the term micro is being misused, for some analysts make a distinction between methods employing weights of 2 to 5 mg. and those of 5 to 10 mg. To avoid much of the ambiguity caused by a not too well-defined prefix, it might be desirable to drop all prefixes and use only the word micro followed by a numeral to show the top range of the weights involved.

Hallett (*79*) in his extensive review published in 1942 listed the basis for selection of certain weights and the accuracy that could be expected, and included detailed descriptions of most of the apparatus and methods of organic microanalysis available then. This review is therefore limited to papers published since 1942. It is somewhat surprising that during this period, which included World War II, considerable strides have been made in this country. Our supplies of apparatus, particularly microbalances, had been cut off, and it was only through the efforts of our American laboratory supply houses, apparatus, and balance manufacturers, and glass blowers that we had available the microchemical equipment required for the expansion of microchemical laboratories. For this an acknowledgment is due.

BALANCES

Few changes, if any, have been made in balances in the past few years, except for the development of the modern quartz microbalance. In 1942, Manigault and Tsai (*153*) developed such a balance with a magnetic compensator. Later in 1943 Nanjundayya and Ahmad (*161*) developed a quartz torsion balance suitable for loads up to 0.5 mg. with a sensitivity of 0.0025 mg. In 1944 Gulbransen (*77*) reported the construction of a quartz balance, to be operated in a vacuum, having a sensitivity of 0.3×10^{-6} gram with fairly large samples.

In 1947 Kirk, Craig, Gullberg, and Boyer (*120*) reported the development of a quartz balance which could handle loads up to 300 micrograms and had a sensitivity of at least 1 minute of arc per 0.005 microgram with loads of 0.1 to 0.2 gram. This ultramacrobalance is said to be more rapid and reproducible than the standard microchemical balance and free of vibration effects. These ultramicrobalances with high sensitivity have been used principally in inorganic chemistry.

In 1947 Stock and Fill (*225*) reported the development of an all-glass, oil-damped semimicrobalance. The balance did not have great accuracy, but it was rapid and filled a definite need. Mettler has developed a semiautomatic semimicrobalance of one-pan construction with a constant load (*6*). A counter automatically totals the weights removed to compensate for the object weight; the decimal weights are obtained by means of an illuminated projected scale. If it is like its counterpart, the macrobalance, one of the few objections will be that it cannot be used with a tare.

For the most part, balances of domestic manufacture in use in organic microanalysis are not air-damped. In Europe, nearly all microbalances appear to have an air-damping system, and on the Continent a multirider control is used in addition. The Bunge microbalance uses air damping beneath the pans, whereas the Sartorius uses overhead damping, for which it is claimed there is less chance of dust entering the air chamber (*15*). Although air-damped, the British Oertling balance does not use the multiple rider.

An American microbalance of new design, the first in some years, is now under test, and probably will be made available in the near future. An outstanding feature is the short-arm beam, which helped to make the Kuhlmann balance so popular.

Whether or not it will be possible to construct a fast and accurate balance built on electronic principles, either magnetic or piezo effect, is still speculative. Clark (*39*) has described one which employs a controlled magnetic lifting device that compensates for the sample load, making the instrument in a sense a null instrument. It is claimed that a load of 1 microgram can be measured with the balance.

A discussion of the accuracy and the reliability of various kinds of balances will not be attempted here, as such studies are now being made by the AMERICAN CHEMICAL SOCIETY'S committee on microchemical balances. Martin (*156*) discussed the different types of balances, the qualities of a good balance, and possible errors. Corwin (*43*) in 1944 made a report on the errors of the microbalance, and described methods for locating and reducing the magnitude of these errors. In 1943 (*191*) the committee on microchemical balances published results which serve as a guide for measuring the performance of an analytical balance.

To increase the speed of the Kuhlmann balance, Tuttle and Brown (*234*) developed a device for projecting a magnified image of the pointer scale.

Wilson (*257*) has listed major factors to be considered as sources of error in microweighing, and has discussed the precautions necessary for cleaning the microbalance.

ELEMENTAL ANALYSIS

CARBON AND HYDROGEN

Micro- or macrodetermination of carbon and hydrogen by catalytic combustion has been a somewhat empirical procedure. In most determinations, it is possible either to reduce the number of variations that can occur and so take measures to ensure that they are controlled during the analysis or to test the end products or residues for completeness of recovery of materials. This cannot be done with the carbon and hydrogen microdetermination by catalytic combustion. The only alternative, after everything appears to be in proper working order, is to use a sample of known purity. If the results are right, the unknown sample is analyzed, and this is followed by another analysis of the known standard. Unfortunately, even this may not succeed; in many cases although the theoretical results for the carbon and hydrogen of the standard were obtained, the results for the carbon and hydrogen of the unknown were low. There can be many causes for this error. A principal one is that the standard material is not similar enough in structure and composition, both of which materially affect the completeness of the burning of the sample to carbon dioxide and water.

Although this determination is one of the oldest and most frequent of microchemical operations, when microchemists were questioned (*253*) as to the microchemical procedure that should be first investigated with the object of developing a standard method of analysis, a study of the carbon and hydrogen analysis was almost a unanimous choice. As in other microprocedures, there has been a definite trend on the part of many microanalysts to use semimicromethods where possible, with a hope for the elimination of many of the errors that are so easily encountered in microanalysis.

There is considerable variation of opinion as to combustion-tube packing, rate of oxygen flow, and temperature of the combustion. Belcher and Spooner (*16*) advocated high temperatures (800° C.) and a rapid flow of oxygen (500 ml. per minute), with silver wool to absorb the interfering acid gases. For combustion at 195° C. of compounds containing nitrogen in addition to halogens and sulfur, Ingram (*105*) has attributed errors to the inefficiency of granular lead peroxide. He believes that best results can be obtained if the filling consists of pumice impregnated with silver vanadate instead of copper oxide and lead chromate or platinum contacts. He reports good success at 300° C. with ceric oxide deposited on silver chromate. These low temperatures of combustion are little used in this country; however, there has been some controversy concerning the temperature for both volatilizing and burning the sample. Although many prefer to keep the temperature at 650° to 750° C. (*40, 55, 83, 96, 219*), there is a trend toward increasing it, even as high as 1000° C. (*8, 232*). The need for a preheater or preburner is also doubtful. It is likely that for standard analyses they will be eliminated, with the use of a constant blank for a given supply of oxygen.

It has been known for many years that during the combustion in oxygen nitrogenous compounds produce oxides of nitrogen. Heron (*86*) claims that practically all the nitrogen of nitro compounds exists as oxides after the combustion and that 1 to 40% of the nitrogen not attached to oxygen in the compound is converted to oxides. The incomplete removal of these oxides of nitrogen is a source of error in the carbon analysis. The customary method for their removal is to pass the products of combustion over lead peroxide maintained at constant temperature. Heron (*87*) found that lead peroxide used in tubes either as lead peroxide–asbestos or in the granular form gave high carbon values. To effect a better removal of the nitrogen oxides, a liquid scrubber was placed between the hydrogen (water) absorber and the carbon dioxide absorber. Heron (*87*) used chromic-sulfuric acid as the scrubbing liquid. The use of a liquid absorber for oxides of nitrogen in organic combustion analysis was suggested by Elving and McElroy (*52*) in 1941, and Horning (*96*) reported best results with it; yet it has not been generally accepted here. In Europe, Etienne (*55*) reported good results, and Belcher (*15*) found that many of the microchemical laboratories on the Continent were using the liquid absorber.

A dry absorber for the oxides of nitrogen, which unlike lead peroxide operates at room temperature, is Hopcalite. This was reported as early as 1937 (*44*) by Corwin, who is still using it in his carbon and hydrogen combustion trains. Hopcalite, however, has never been widely accepted; consequently, few have commented on it.

The automatic carbon and hydrogen combustion furnaces have been the subject of much controversy. Today they have been fairly well accepted. Clark and Stillson (*40*) and Horeischy and Bühler (*95*) have described semi- and fully automatic combustion apparatus, adding to the already extensive literature (*40, 219*). The rate at which the burning or vaporizing furnace should move has not yet been settled, and consequently the only commercially available automatic device is provided with a variable-speed control. Many analysts, especially those using less than 10-mg. samples, heat the packed portion of the tube with an electric furnace, but some still prefer to vaporize the sample with a gas heater. In this country, we have more or less accepted automatic burning for carbon and hydrogen analysis, but English analysts have not accepted it. German (*15*) laboratories have adopted it almost 100%. In one laboratory, they have gone so far as to develop an automatic chamois wiper for the absorption tubes.

No attempt is made here to discuss tube fillings. Although they are varied, they are all essentially similar to the original Pregl filling. It is hoped that the work on standardization of methods may lead to some uniformity. The size of the combustion tube is also undergoing considerable discussion. Although the committee on standardization of microchemical apparatus will recommend a size for use in microanalysis (up to 10 mg.), it has not received complete replies to inquiries regarding the size of the tube in general use. Among analysts who use semimicrosamples (20 mg.) or larger there is a definite trend toward using a tube of small inside diameter, one closely approximating that recommended for microanalysis.

For the regulation of gas flow, Furter and Steyermark (*60*) have described an apparatus which has an attached scale and uses no metal parts; the train uses the Mariotte bottle. Irimescu and Popescu (*109*) have proposed burning under positive pressure, with the combustion train attached directly to a reducing valve on a gas cylinder instead of a gasometer and pressure regulator. Goulden (*74*) uses an automatic regulator and manometer. It is possible that these systems will gain in acceptance, especially if the combustion is made with a definite volume of gas.

Several new absorption tubes have been proposed. MacNevin and Varner (*152*) have described the use of absorption tube tares without wiping, which permits the use of Pyrex tubes. Lacourt (*129*) has described a Friedrich type of absorber and has given methods of sealing. Langer (*133*) has developed a tube which eliminates the air jacket of Friedrich and the cap and sleeve of the Abrahamiczik tube.

Some compounds do not lend themselves readily to the catalytic analysis of carbon and hydrogen, particularly those of explosive nature and in some cases long-chain fatty acids. For these it is becoming a practice to determine the carbon only, using a wet combustion procedure. A simple method for 15- to 20-mg. samples is the adaptation of the Van Slyke manometric amino nitrogen apparatus, using chromic oxide, potassium periodate, and fuming sulfuric acid in phosphoric acid as oxidants, then measuring the volume of the carbon dioxide gas formed.

More recently, Houghton (*99*) suggested an apparatus for samples containing 2 to 5 mg. of carbon and an oxidizing solution of phosphoric, sulfuric, and chromic acids. The liberated carbon dioxide is trapped in a barium hydroxide solution, the excess of which is back-titrated with standard acid. Oberhauser (*171*) and others have conducted the oxidation with potassium persulfate and silver sulfate, trapping the carbon dioxide in 30% potassium hydroxide, noting the increase in weight or in 0.5 N potassium hydroxide, and determining the carbon dioxide by Winkler's method.

NITROGEN

Determination of nitrogen has been the subject of a large number of papers in the microchemical as well as in the macrochemical field. The object is to devise a simpler and more rapid but accurate method. Because of the simplicity of the apparatus and other desirable features, the Kjeldahl method has been well received. Its use in the determination of nitrogen has been largely limited to naturally occurring mixtures, principally in the field of biochemistry (*9*). For the analysis of pure nitrogenous compounds, this method has been more restricted, and has been accepted with some skepticism, as it has been demonstrated time and again that nitrogen cannot always be completely recovered from certain refractory types of compounds, chiefly those containing heterocyclic nitrogen.

The controversy over the ideal combination of catalysts of the past decade is still going on. Beatty (*11*) has advocated a large amount of crystalline anhydrous copper sulfate, the undissolved crystals serving as boiling chips, and has advised the addition of selenium for semimicrosamples. Sobel, Mayer, and Gottfried (*211*), in their adaptation of the Kjeldahl method for urea and other nitrogenous compounds, use the same flask for digestion and distillation and are able to determine total nitrogen in as little as 0.01 ml. of blood. Kaye and Weiner (*112*) have modified the method of Clark (*38*) by using the mixed indicator of Ma and Zuazaga (*149*), which consists of bromocresol green and methyl red. Others (*172*) have since varied the ratio of the indicator to the dye in this mixture. Kaye and Weiner (*112*) advocate overtitration of the trapped ammonium solution with strong standard acid and back-titrating with a dilute alkali. Cole and Parks (*42*) have confirmed the observations of others that copper as a catalyst used in the absence of selenium and mercury gives low results, while mercury and selenium oxychloride catalyst give excellent recoveries on all nitrogenous compounds except those containing a nitrogen-to-oxygen or a nitrogen-to-nitrogen linkage.

Portner (*183*) has outlined a simple oxidation mixture which omits a metal catalyst. He uses bromine and 30% hydrogen peroxide in the presence of sulfuric acid. Care must be exercised, however, to prevent overheating and consequent carbonization. There is a definite trend toward the omission of all metallic catalysts except mercury, with a more exact control of the amount of salts and acids to be used in the digestion mixture. White and Secor (*248*) have shown that with this mixture the nitrogen can be quantitatively recovered from tryptophan and gramicidin without a hydriodic acid pretreatment. Ballantine and Gregg (*9*) use only phosphoric acid, sulfuric acid, and solid potassium persulfate in the digestion and have reported excellent results if the mixture is kept almost anhydrous to prevent the solution of the persulfate. They have also adapted the use of biiodate in the iodometric titration of the liberated ammonia. Brüel *et al.* (*26*) have given excellent directions for conducting micro-Kjeldahls. In addition to the complete description of microapparatus, they have discussed catalysts, and although they were forced to use selenium because of the conditions of their experiments, they indicate that they were never able to account for more than 70% of the nitrogen of a refractory material like pyridinium-zinc chloride $(C_5H_5NHCl)_2(ZnCl_2)$. The proper conditions for the digestion are still uncertain, as pointed out by Kirk (*119*), who believes that enough attention has not been given to the salt concentration, the time of digestion, and the control of the selenium as a catalyst. For use in aeration microtechnique, Sobel *et al.* (*210*) have described two new types of absorption tubes. One is a sealed-in bubble tube applicable to 10 to 200 mg. of ammonia; the other is an adaptaton of a conical centrifuge tube usable in the determination of 1 to 10 mg. of ammonia.

DUMAS NITROGEN

The Dumas procedure is perhaps still the most generally accepted method for determining nitrogen in all types of nitrogenous organic compounds. Few modifications in the procedure have been proposed in the past few years. Instead, attention is centered on improvement of the apparatus, both the combustion tube and the nitrometer.

Zimmermann (*269*) designed an apparatus in which he was able to complete an analysis of materials such as atropine satisfactorily in 25 minutes. With his apparatus the combustion takes place automatically. Copies of his mechanized Dumas apparatus are to be found in many of the German microchemical laboratories. He used solid carbon dioxide as the source of the inert gas, a practice which is becoming more and more popular, both here and abroad. The source and method of manufacture of this material are often of great importance. In the author's laboratory, it was observed that when the solid carbon dioxide was obtained from fermentation, the amount of nitrogen trapped with it made it utterly unsuitable for use in the Dumas method. Korshun and Hel'man (*127*) have described the apparatus using the Kipp generator, an electrical heater for the long burner, and a gas sample burner. Evidence that the minimum temperature for heating the sample tube is 650° C., with low and erratic recoveries of nitrogen below this temperature, has been presented recently in unpublished reports of Association of Official Agricultural Chemists referees.

Weygand (*246*) called attention to the fact that chance introduction of foreign material, such as that from rubber connectors, into the apparatus should be guarded against, and suggested an apparatus with glass-joint connections.

Gonick *et al.* (*66*) proposed an all-glass improved Dumas apparatus operated at 750° C. To ensure the complete combustion of refractory materials, the products of combustion and oxygen are recycled through the combustion tube until constant residual volume is obtained.

Kirsten (*121*) has proposed one of the first truly radical changes in the Dumas method. The temperature of the combustion is not sufficiently high for all types of compounds, but with copper filling temperatures much above 800° C. cannot be used. Kirsten, using a quartz tube with ground joints, suggests as the permanent filling nickel–nickel oxide, which allows the use of temperatures of 1000° C. and with backward stream washing results in a saving of time and longer life of the filling. The temporary filling of copper oxide is held in a quartz capsule.

To prevent possible adherence of gas bubbles on the surface of the mercury in the nitrometer, Pomatti (*182*) uses a small curved piece of iron wire, which is floated on the mercury and moved over the surface by means of an external magnet to sweep off any adhering gas bubbles. Müller (*160*) carried Weygand's idea one step further by developing a new azotometer, which eliminates rubber leveling tubes or connectors. The nitrometer is a compact instrument with the alkali chamber, gas buret, and leveling device all interconnected by glass. To avoid the most common sources of error of the nitrometer, Stehr (*216*) has replaced the conventional stopcock with a ball and socket valve, which offers many advantages. To eliminate much of the difficulty encountered with the precision stopcock for controlling the flow of carbon dioxide from combustion tube to nitrometer, Hershberg (*88*) devised a needle valve with glass seat and mercury packing. A new valve made entirely of stainless steel, which is rugged yet sufficiently light, has now been designed.

A great deal of difficulty has been experienced with the limestone-Kipp generator as a source of nitrogen-free carbon dioxide, especially during the war years, when a supply of satisfactory marble was nonexistent. Pagel (*175*) has designed a generator which uses pure bicarbonate as the source of carbon dioxide. The apparatus supplies a good nitrogen-free carbon dioxide gas, but it is fragile and difficult to change.

Determination of nitrogen existing as nitrates is still a serious problem, partially solved by the adaptation of the Devarda method by Kieselbach (*116*) for determining 0.05 milliequivalent of nitrates. Leithe (*137*) has suggested an indirect method whereby the nitrate oxidizes ferrous iron of known titer, and excess of ferrous iron is measured with standard dichromate. Genevois (*63*) has outlined the formation of various nitro compounds, many of which can be analyzed by the titanium trichloride reaction.

HALOGENS

Determining halogens constitutes one of the major tasks of microchemists, as such analysis is important from the standpoint of identifying organic compounds and indicating their purity. In many compounds, determination of halogens is a fairly simple matter, especially if they exist in an ionic form. For the more refractory materials, the catalytic oxidation method of Pregl is still much in vogue, but many compounds are resistant to this treatment. As a result, many still prefer the Parr peroxide bomb method or the Carius method, which are generally known and so are not discussed here. Both methods, however, introduce such a high concentration of salts and other interfering materials into the solution that subsequent titrimetric procedures become difficult.

Elving and Ligett (*51*) proposed a method for decomposing fluorides and other halogen organic compounds by heating them with an alkali metal in an evacuated tube at moderate temperatures, forming the alkali metal halide, which can then be determined by conventional means. This method was described by Zimmermann in 1928 for the destruction of sulfur compounds, and also by Bürger (*27*). The potentiometric identification of the end point of the halogen titration [for which Dean and Hawley (*47*) and Northrop (*170*) have described electrical setups] appears to be a definite advance.

Irimescu and Chirnoaga (*107*) have adapted the method of Stepanov to microprocedure. This consists of converting the halogen of the organic compound to the sodium salt by heating it with a mixture of absolute ethyl alcohol and metallic sodium. Sisido and Yagi (*206*) digest the sample containing about 2 mg. of chlorine with an excess of sodium in butyl or amyl alcohol and titrate the resulting chloride ion with standard silver nitrate, with phenol blue as the adsorption indicator. Jurecek (*110*) decomposes the organic halogen compound by catalytic oxidation and passes the gaseous products over hot sodium carbonate, which picks up the acidic gases of bromine and chlorine to form the sodium salt. Iodine gases are trapped by heated silver dispersed on magnesium oxide. Peel, Clark, and Wagner (*177*) prefer the Parr peroxide bomb for decomposition and formation of the alkali salt. They strongly disapprove of the volumetric Volhard method for iodine and bromine analysis, because the end point is not certain except with too strong reagents. For liquid samples, they have proposed the use of gelatin capsules in the bomb. Christensen (*35*) has developed a micromethod for organic iodine based on its oxidation to iodate with permanganate. The iodate is measured in terms of liberated iodine with standard thiosulfate.

Harlay (*80*) has proposed a quantitative method for determining iodine which uses fluorescein not as an indicator but as a reagent. This is based on the fact that the diiodo derivative is nonfluorescent in ultraviolet light and its formation is controlled by the pH of the solution. By measurement of the decrease in fluorescence of the reagent, the amount of halogen present can be determined. The sensitivity of the test can be increased sixfold by converting the iodine to iodate and then liberating iodine from potassium iodide, thus increasing the amount of iodine six times over the original quantity. Dubouloz *et al.* (*48*) uses thiofluorescein, the synthesis of which is given as a colorimetric reagent for iodine. One atom of iodine in acid solution and two atoms in alkaline solution oxidize it to a colorless product. Its absorption curve shows a maximum at 5850 Å.

Shahrokh (*205*) has modified the chlorate digestion method for determining iodine in biological materials so that larger sample weights may be taken and the interference of iron and manganese eliminated. Teston and McKenna (*232*) use a high-temperature oxidation (1000° C.) for the destruction of halocarbon and are able to determine fluorine, chlorine, and carbon simultaneously. Small quantities of chloride ions can be determined readily by the method of Leithe (*138*), in which the chloride ion reacts with silver chromate to yield silver chloride and a soluble chromate. The chromate is easily titrated with dilute ferrous sulfate solution.

OXYGEN

A microchemical method which permits the direct determination of oxygen in organic compounds is perhaps one of the greatest advances in analytical chemistry for many years. It is now past the experimental stage, and its use will be demanded along with all other accepted methods for ultimate analysis as soon as there are definite indications that satisfactory equipment can be furnished. The high temperatures require a furnace that is not so easy to build as those for carbon and hydrogen, sulfur, and the halogens, and it may require some time before these furnaces become available.

Elving and Ligett (*50*) have presented a historical review of the methods used for the determination of oxygen, with special emphasis on the hydrogenation method of Meulen.

The method that has won great popularity for the direct determination of oxygen is the one first developed by Schütze (*202*) and later modified by Zimmermann (*271*) and Unterzaucher (*235*). It is the latter's modification that has been developed in this country by Aluise *et al.* (*5*). The essential features of this determination consist in decomposition of the sample in a stream of nitrogen made oxygen-free by passage over heated copper and the ultimate conversion of all the oxygen of the organic compound to carbon monoxide by passing the gases over heated charcoal which must be maintained at 1100° C. The amount of oxygen is then determined from the carbon monoxide, after it is converted to carbon dioxide with iodine pentoxide. The carbon dioxide is measured titrimetrically in terms of the liberated iodine or gravimetrically after absorption in Ascarite.

Zimmermann (*271*) uses an automatic burning furnace. The carbon monoxide is oxidized quantitatively at room temperature by means of a special preparation of iodine pentoxide. Unterzaucher prefers to oxidize the carbon monoxide with iodine pentoxide heated in an acetic acid bath and determine the liberated iodine titrimetrically. If the amount of iodine liberated is low, it is oxidized to iodate and thereby amplifies the titer. The nitrogen is purified at room temperature by using copper which has been reduced with hydrogen just before use. Aluise has described the construction of the furnaces for the destruction of the organic sample and for the conversion of carbon monoxide to dioxide. Details are given concerning the selection of the carbon and the iodine pentoxide. Somewhat less accuracy and precision have been obtained than those now obtained for carbon and hydrogen analyses. The presence of sulfur, nitrogen, and halogens does not interfere, and there is no problem of catalyst poisoning. Walton *et al.* (*241*) have given complete details for the construction of the glass apparatus and the furnaces. They have found helium superior to nitrogen for providing the inert atmosphere of the combustion. For small amounts of oxygen, the carbon monoxide formed is measured colorimetrically with indication gel. Korshun and Hel'man (*126*) have also described a method similar to that of Unterzaucher.

Spooner (*215*) has attempted to avoid the high temperature of 1200° C. required to reduce carbon dioxide to the monoxide with carbon by activating the carbon with sodium oxide. He was successful in doing this at 800° C. for one determination, but the carbon deposited from the sample on the activated carbon caused it to cease to function.

SULFUR

In the past few years many have reported a "good" sulfur method. Zimmermann (*268*) developed a method based on that of Bürger. Potassium sulfide is formed by decomposing the organic sulfur compound with liquefied potassium. The excess potassium is destroyed with methanol, and the sulfide is converted first to hydrogen sulfide and then to sulfur. Later he trapped the hydrogen sulfide in cadmium acetate and determined the sulfur iodometrically (*270*).

Klein (*122*) has developed a colorimetric method for determining sulfur after it has been precipitated as benzidine sulfate. The precipitate is dissolved, diazotized, and coupled with Britton and Marshall's reagent to give a dark purple color, which can be measured in a photoelectric colorimeter. The method is said to be accurate to 0.05 to 0.150 mg. of sulfur.

To convert all the sulfur to sulfur trioxide, Ingram (*104*) conducts the catalytic oxidation of the sample in a stream of oxygen saturated with water vapor. After a neutral solution of basic mercuric cyanide is added, the sulfur products of the combustion can be determined titrimetrically with standard barium chloride. Any barium chloride in excess of the sulfate will react with the basic mercury salt, liberating hydroxyl ions which can be shown with an acid-base indicator. Korshun and Hel'man (*128*) decompose the substance in a stream of hydrogen over a glowing platinum catalyst. The sulfur is determined iodometrically after the hydrogen sulfide is absorbed in a zinc sulfate–acetic acid solution.

Irimescu and Chirnoaga (*108*) also decompose the sample in an atmosphere of hydrogen, but their contact catalyst is finely divided platinum deposited on small quartz tubes. They point out that a temperature of 1000° to 1100° C. is required for the conversion of sulfur of organic components to hydrogen sulfide. The catalyst becomes inactive as carbon deposits on it. The sulfur is determined titrimetrically. After the gas is absorbed in a silver nitrate solution and the silver sulfide precipitated, the excess silver is determined by Volhard's method.

Yagi and Egami (*265*) decompose the sulfur sample in a sealed tube containing fuming nitric acid and sodium chloride (Carius) and then determine the soluble sulfate by the method of Hinman. Horeischy and Bühler (*94*) also use the quartz bomb and nitric acid for decomposition, but determine the sulfur in the reaction products as sulfuric acid by evaporating on an evaporating block at 105° to 110° C. to remove all other acids and titrating with standard potassium hydroxide. Sundberg and Royer (*231*) have described the decomposition of sulfur compounds and the collection of the soluble sulfate with a Grote combustion apparatus. The sulfur is determined titrimetrically with standard barium chloride, dipotassium rhodizonate being used as indicator.

In addition to a scheme of decomposition of organic compounds for sulfur, Alicino (*1*) has proposed a procedure for the identification of the dipotassium rhodizonate end point with standard barium chloride.

Ogg, Willits, and Cooper (*174*) have described a titrimetric technique for identification of the end point in the volumetric determination of soluble sulfates with barium chloride and dipotassium rhodizonate. They have eliminated one of the principal sources of error in using this indicator and have suggested means of avoiding a correction factor when small amounts of sulfur are determined as sulfates. Steyermark, Bass, and Littman (*220*) have applied the titrimetric technique of Ogg *et al.* to the analysis of organic compounds decomposed by the Carius method.

Wagner and Miles (*239*) have described a method using the Burgess-Parr oxygen bomb. The resulting sulfuric acid is determined with standard alkali after the sulfur is first precipitated and separated as benzidine sulfate.

Freri (*58*) has found that when the sulfur is determined gravimetrically as barium sulfate, the addition of 10% ethyl or amyl alcohol to the aqueous solution in which the precipitation is made facilitates the subsequent handling of the barium sulfate. As the precipitate does not lump, a simple spray or jet of wash water may be used.

Krocker filters the precipitated barium sulfate with a sintered-glass crucible (*15*). The solution is decanted, and the precipitate is washed directly from the precipitating dish to the filter according to macrotechniques. Although this is a rather startling procedure, less loss of sulfate is reported than when elaborate precautions are taken by using filter sticks, filter beakers, and the like.

GROUP ANALYSIS

ALKOXYL

Many workers have made suggestions for modification of the method for determination of alkoxyl to overcome erratic results and operational difficulties, in order that its usefulness can be extended to a wider variety of compounds and greater accuracy can be obtained with a simple rugged apparatus. White (*249*), using the method of Viebock and Brecher, redesigned the apparatus of Zacherl and Krainick (*267*) for the semimicrodetermination of both alkoxyl and halogens. Saccardi (*192*) modified the Zeisel apparatus to prevent bumping or surging of the hydriodic reaction mixture by leading the carbon dioxide through a capillary heated at 200° C. The hot gas is sufficient to keep the reaction mixture boiling smoothly. White (*247*) has discussed the effect and use of washers for scrubbing the distilled vapors of the alkoxyl analysis. Owing to the solubility of methyl iodide and its subsequent reaction with thiosulfate, thiosulfate used alone gave low values for methoxy- and methylimide. Ethoxyl- and ethylimide are not subject to this loss. This difference furnishes a simple means for rapid distinction between ethoxyl and methoxyl, provided a good washer can also be used. White has shown that the solubility of methyl iodide can be minimized by dissolving the thiosulfate in saturated sodium chloride or by adding cadmium sulfate to the thiosulfate solution. He has also shown that other wash waters containing phosphorus suspensions or 0.5% sodium carbonate are satisfactory.

Houghton (*100*) designed an apparatus, a modification of Clark's (*37*), which can be left unattended and still give reliable results. A rapid stream of carbon dioxide is introduced at the bottom of the reaction flask, and the sample spoon is so placed as to serve as a boiling chip. These, plus a rapid boiling rate, prevent bumping. To prevent distillation of the hydriodic acid, a water jacket is mounted on the tube. The trap holding the scrubbing liquid is so designed that the spent liquid can be easily removed and the trap refilled. An analysis is said to be completed every 20 minutes. In an effort to separate or identify the alkoxyl as methyl or ethyl, Houghton (*98*) substituted capillary U-tube immersed in acetone–solid carbon dioxide for the spiral trap of the previous apparatus. Nitrogen is substituted for carbon dioxide, and the alkali halides are condensed in the U-tube. The alkyl can be identified by density measurement accurate to 1%, but this requires a minimum of 30 mg. of sample. Boiling point determinations require only 3 mg. of sample, with a possible 5% error.

In the analysis of acetals and easily volatilized alcohols, low ethoxy values are often encountered. Hoffman and Wolfrom (*93*) attributed this to the loss of these volatiles from the reaction mixture after saponification, before they had reacted with the hydriodic acid. To avoid this loss, they designed a sample holder, for both liquids and solids, in which the entire sample is in contact with the reaction mixture long enough for the formation of the alkyl halide. To aid in the complete solution of the material during alkoxyl analysis, the solids sample holder or cup is sealed with a film of tartaric acid, making it possible to introduce the sample below the surface of the reaction mixture. They have designed a new type of receiver that does not require a spiral for washing the alkyl halide from the gas stream. The authors claim good results.

Steyermark (*218*) also calls attention to the low alkoxyl values obtained with Pregl's apparatus for the analysis of volatile compounds, esters which split off the alcohol on immediate contact with hydriodic acid, or compounds with more than one methoxyl group. To avoid this difficulty, he has constructed an all-glass apparatus combining the essential features of the Fürter apparatus, which employs double distillation and is used successfully for the analysis of either alkoxyl or alkimide groups in volatile substances, and the Elek apparatus, which utilizes a water-cooled reflux condenser and a more efficient absorption tube for the alkyl halide. The reaction mixture is allowed to stand for some time before heating. Preparation of the hydriodic acid is of special interest. Steyermark is one of the first to suggest that a colorless acid of constant boiling point is unnecessary. His reagent is prepared by merely refluxing (air condenser) ordinary reagent grades of hydriodic acid for about 2 hours while a stream of carbon dioxide or nitrogen is bubbled through. The color of the resulting acid is not important, for even dark grades give no blank.

ACETYL

Clarke and Christensen (*41*) have supplied a simple procedure for determining acetyl groups in acetates of sugars and glucosides. The sample is placed in an Erlenmeyer reaction flask with a few milliliters of ethyl alcohol and a known volume (4 ml.) of 0.045 *N* sodium hydroxide. The mixture is shaken for 4 to 24 hours, and the excess of alkali is titrated with 0.05 *N* sulfuric acid to a phenolphthalein end point.

An improvement of the Kuhn-Roth apparatus for determining acyl groups has been made by Wiesenberger (*251, 252*). By redesign of the condensers and shape of the reaction vessel, it is possible to obtain in a few minutes a distillate free of high-boiling acid, and the hydrolysis can be accomplished with phosphoric instead of the usual sulfuric or *p*-toluenesulfonic acids. This apparatus permits determination of the total acetic acid with single distillation of 30 to 35 ml. One determination after the other can be made without cleaning. A single determination requires about 75 minutes.

Alicino (*2*) reports that most *O*-acyl groups can be determined in a manner similar to that of Clarke and Christensen by dissolving the sample in acetone instead of ethyl alcohol and hydrolyzing at room temperature for 2 hours with an excess of 0.01 *N* sodium hydroxide. The excess sodium hydroxide is determined by titration to a phenol red end point that must remain distinctly yellow for at least 2 minutes. A blank is run with the acetone alone.

HYDROXYL

In the group analysis of organic compounds, methods for determining the hydroxyl content have received attention. Stodola (*230*) was the first to reduce to a micro scale the esterification with acetic anhydride-pyridine mixture. Petersen, Hedberg, and Christensen (*178*), using sealed reaction tubes, applied this technique to a large number of typical alcohols and phenols. Ogg, Porter, and Willits (*173*) have modified their macroprocedure by using a reaction vessel with glass joints.

AMINES AND AMINO ACIDS

Plein and Dewey (*180*) have proposed a method for identifying organic aliphatic amines and some mixtures of amines as their diliturates. Woiwod (*260*) has developed a paper chromatographic method for separating some compounds containing α-amino nitrogen and then determining them by a colorimetric method.

Aqvist (*7*) has also developed a colorimetric method, which measures as little as 0.05 to 0.20 mg. of alanine. Virtanen (*237*) estimates amino acids by converting them to a volatile aldehyde and then to the acid by ninhydrin oxidation.

A paper by Konikov (*125*) describes a new amino acid manometric apparatus. The Hempel pipet is eliminated, the barometric manometer is replaced by a McLeod gage, no separate blanks are required, and the mercury of the manometer never falls into the reaction vessel. The apparatus is smaller and more solid than the Van Slyke apparatus.

ALDEHYDES AND KETONES

Determination of small quantities of various ketones has been described by Sozzi (*213*), who separates them by precipitation with 2,4-dinitrophenylhydrazine. For a mixture of two aldehydes or two ketones, Brandstätter (*23*), using the glass powder method of Kofler, measures the optical refraction of the resulting hydrazones from this reaction. Genevois (*62*) measures the aldehydes and ketones, and identifies them by the melting points of their nitro derivatives.

ANALYSIS OF MIXTURES

The use of microchemistry has been extended, and like macroanalysis, it is now used for the quantitative measurement of materials in mixtures as well as for the ultimate analysis of pure compounds.

ALCOHOL

Stodola (*229*) has devised a direct method based on the sensitive iodoform test of Lustgarten, which makes possible the estimation of alcohol in small amounts of material. McNally and Coleman (*151*) and Chaikelis and Floersheim (*32*) have described volumetric oxidation methods for ethanol in as little as 0.1 ml. of sample. Henry and Kirkwood (*85*) oxidize the ethyl alcohol to acetic acid and determine it colorimetrically with *p*-hydroxybiphenyl. For mixtures of esters of methyl and ethyl alcohol, Ionescu-Matiu and Popa (*106*) saponify with potassium hydroxide, distill the liberated alcohol, and titrate it with potassium dichromate in the presence of methylene blue leuco base.

ORGANIC ACIDS

In the analysis of acids by micromethods, procedures have been outlined for citric acid (*24, 184*), and for hydrocyanic acid in blood, in plant tissue, and in solution (*59, 64, 185*). Formic acid is determined by the reduction of mercuric chloride (*75*), by colorimetric determination of formaldehydes formed from the acid (*76*), and by a bromine oxidation method similar to the acetyl method (*3*). Chromatography has been employed to determine lactic acid and succinic acids in foods (*36*).

SUGARS

Few recent papers on sugar analyses deal with small samples. Interest appears to be centered in the accurate accounting of minute amounts of the sugars. These papers (*159, 181, 193, 236, 261*) include colorimetric methods for traces of glucose, methods for total sugars with the Suff-Scharol reagents, the Bertrand and Somogyi methods, and the Hawthorne paper chromatography method for separating and estimating (*82*) sugar.

VITAMINS

The assay of various vitamins has been microchemical only on the basis of the small amounts of the constituents sought and not on the size of the sample. Some of these methods have been for B_1 (*92, 196, 238*) and for C (*29, 132, 146, 186*).

FATTY ACIDS

Stetten and Grail (*217*) have described a titration method applicable to the analysis of 8- to 20-mg. samples of fatty acids. Schmidt-Nielson (*199*), after saponification, isolates the fatty acid with toluene and titrates it with 0.02 *N* base to a thymol blue end point. Gorbach (*68*) describes a fat extraction microapparatus suitable for the microanalysis of fat in oilseeds. A method for estimating oleic and linoleic acids which consists in the oxidation of the acids to dihydroxystearic and satinic acids, respectively, has been described by Gorbach and Malissa (*72*). The oxidation products are quantitatively separated and identified.

Spatt and Schneider (*214*) have used the partition coefficient of organic acids between ether and water for their identification. The amount of organic acid in the water is determined by titration.

Hill (*90*) has developed a colorimetric method for estimating the amount of fatty acids, esters, or methylated fatty acids by forming hydroxamic acid. A colored complex can be produced with alcoholic ferric perchlorate. For determining volatile fatty acids in blood, McClendon (*150*) has developed a special still for steam distillation. Distillation curves are presented for volatile acids found in blood filtrate.

SAPONIFICATION

Until recently, microchemists have been reluctant to attempt the quantitative saponification of esters, regardless of whether they exist as pure compounds or as mixtures in natural fats and oils. The need, however, has been great, for it offers an excellent method for determining molecular weight of pure material. Mitchell, Smith, and Money (*158*) have developed a method in which the saponification is conducted in a closed system with 2 *N* sodium hydroxide. The authors specify alcohol containing 10% water, but do not discuss this important point. They do observe and discuss steric hindrance. Marcali and Rieman (*154*) and Ketchum (*115*) have proposed a method using the double indicator method of Rieman. It is applicable to decigram, centigram, and milligram samples, but they recommend the decigram sample.

One of the principal difficulties in microsaponification is to have enough alkali in the reaction mixture to ensure complete de-esterification; another is to measure the excess of alkali with the requisite accuracy. Fischer employs a method for determining acetyl groups which may be applicable to the saponification problem (*15*). The de-esterification is conducted with a large excess of alkali (added as 0.5 *N* sodium hydroxide), which tends to reduce the time and ensure the completeness of the saponification. The large excess of alkali does not interfere, as it is removed by a hydrogen ion exchanger and the sodium salt of the organic acid is converted to the organic acid by the same treatment. The results is that the organic acid sought can be directly titrated. If it does not have a sharp end point, excess of a standard base of low titer can be added and back-titrated with a low titer acid.

DESICCATION

Barraclough (*10*) has presented a list of desiccants and discusses their application. Pavelka (*176*) calls attention to the possible moistening of the dried sample each time the desiccator is opened. To avoid this, it is recommended that the material be dried and stored in a Pregl absorption tube, which permits working with any desired gas, drying at any temperature, and using any vacuum. The drying gases can be dried with any number of desiccants, but phosphorus pentoxide was by far the best of 11 desiccants tested.

In the purification of compounds, many are separated from alcoholic solutions, and some will retain a few molecules of the alcohol, regardless of the drying conditions. A simple but little-known method, the literature reference to which is unknown, is to place such an alcoholated sample in a moist atmosphere, as in a vacuum desiccator containing an open vessel of water, for 8 to 18 hours. Water in the vapor will displace the alcohol, and the moistened sample can then be easily freed of the water by drying. A method of drying analytical samples that is becoming popular is to use as dry an atmosphere as can be obtained rather than a high vacuum. This is best accomplished by placing the sample in a drying chamber and drawing a stream of dry air or gas through the chamber.

GAS ANALYSIS

Nash (*165*) has described an apparatus with which a complete analysis of 0.1 to 1 ml. of a gas sample for such constituents as carbon dioxide, carbon monoxide, methane, hydrogen, and nitrogen can be made with an accuracy of a few tenths of 1%.

Kenty and Reuter (*113*) have described a microapparatus with which the gases are analyzed by physical measurement except for carbon monoxide and hydrogen, which must be removed by oxidation with oxygen and a tungsten filament. The other gas components are measurd by their condensation points, comparison readings of Pirani and McLeod gages, and differences in speeds of flow. Samples consisting of only a few microliters can be analyzed with relatively high accuracy.

For analysis of mixtures of nitric oxide with hydrogen and nitrogen, Smith and Leighton (*208*) have given procedures whereby the nitric oxide is removed by oxygen in the presence of sodium hydroxide. Ammonia can be separated from nitrous oxide by absorption by monochloroacetic acid. LeRoy and Steacie (*140*) use alkaline sodium sulfate to absorb nitric oxide; unlike the previous method, this can be used in the presence of combustible gases. Instead of measuring nitric oxide in gases by the decrease in volume after absorption, Kieselbach (*117*) passes the gas through an alkaline permanganate solution, after which the solution is analyzed by a micro-Devarda method. An accuracy of 99% can be obtained.

For determining carbon monoxide in solution, Smaller and Hall (*207*) use a method based on the amount of iodine, liberated in the oxidation with iodine pentoxide, which can be measured spectrophotometrically at 350 mμ. The method is reliable for concentrations of carbon monoxide as low as 0.005%, and an accuracy of 3 to 10%, depending on the carbon monoxide concentration, can be expected.

Salsbury, Cole, and Yoe (*194*) determine carbon monoxide gravimetrically by absorption on Ascarite after it has been oxidized to carbon dioxide by passing over Hopcalite at 195° C. Analysis of gases containing carbon monoxide in concentrations of 0.002 to 0.1% can be made. A method of analysis for carbon dioxide and oxygen in 0.7 to 0.14 cu. mm. of blood with an accuracy of ±0.6 to ±1.5% is described by Scholander and Irving (*201*). The micrometer buret described by Scholander and Evans (*200*) is used. For determining carbon monoxide in air, Beckman, McCullough, and Crane (*12*) have devised a portable instrument which makes use of two reactions, one between carbon monoxide and red mercuric oxide, yielding mercury vapor and carbon dioxide, and the other between mercury vapor and selenium sulfide. The latter is on a test strip, and as the air containing the mercury flows along the strip, a black coloration is produced. The method is applicable over a wide range of concentrations of carbon monoxide.

Sendroy and Granville (*203*) have applied their method of microanalytical reflectance spectrophotometry to the determination of carbon monoxide in air. A thin layer of palladium chloride on white paper is exposed to the air, and the change in color is measured.

Kinsey and Grant (*118*) have described a method for measuring mustard gas. The gas in amounts ranging from 0.5 to 200 micrograms is absorbed in organic solvents which contain chloramine-T. The residual chlorine is determined iodometrically.

TITRIMETRY

Titrimetric determinations of solutions of acetic acid by acidimetric, potentiometric, and iodometric methods have been compared by Hurka (*102*). The acidimetric method was satisfactory with 0.01 *N* sodium hydroxide, thymol blue indicator, and a final volume not to exceed 35 ml. For low concentrations of the acid, however, the iodometric procedure is highly recommended. Ingold (*103*) recommends that the titration of organic acids be conducted potentiometrically with a glass electrode. By using the buret which he describes, which can be read to 0.0001 ml., and performing the titration in a depression in the glass electrode, 300 to 900 micrograms of an organic acid of molecular weights from 100 to 500 can be determined.

The titrations of extremely dilute chromate solutions with ferrous iron, with a rotating platinum wire as the indicator electrode, has been described by Kolthoff and May (*124*). The method is said to be accurate to within 5% at concentrations of 1 to 2×10^{-4} *M* chromate.

Stock (*223*) has been able to measure the diffusion current of the reagent or of the substance under investigation by adjusting the potential of a rotating microelectrode with a potentiometer. The end point of the titration is located by the intersection of the two straight lines obtained by plotting current reading against buret reading. Some applications are the titration of halides with silver nitrate, arsenious trioxide with potassium bromate, and chromate ions with ferrous iron.

Stock (*224*) has also made microchemical application of the dead-stop end-point titration method, so that it can be used on the one-drop scale. The conditions must be so arranged that the solution to be titrated contains a substance able to destroy the polarization at either electrode. Stock suggests many uses and devices by which depolarization can be maintained up to the end point, such as the titration of thiosulfate ions with iodine. In his paper on microchemical applications of potentiometry (*221*), he gives the design of suitable apparatus for the one-drop scale titration. The rotating dish, vibrating ring, horizontal shaker, and an electrotitrimeter are used.

MOISTURE

The Karl Fischer method is not entirely suitable for determination of low moisture, especially in micro- and semimicrosamples, as the titer of the reagent must be low in order that adequate volumes of the reagent will be required, making differential readings practical. Levy, Murtaugh, and Rosenblatt (*142*), however, have reported satisfactory precision with the Karl Fischer reagent and a small closed system. They found that 1 to 25 mg. of water could be determined with an accuracy of ±20 to 100 micrograms.

Lindner (*144*) recommends the use of naphthyl oxychlorophosphine. One gram of the reagent will measure as much as 25 to 30 mg. of water. The reaction is best carried out at 105° C. Lindner (*143*) has also shown that cinnamyl chloride, used by some for the microdetermination of moisture, may give high values under certain conditions, owing to the formation of hydrochloric acid by the cinnamic acid formed and the acid chloride. Gorbach and Jurinka (*71*) have adapted the calcium carbide method of Jakawenko to microanalysis. The acetylene formed by the moisture present is measured volumetrically.

PHYSICAL METHODS

BOILING POINT

García (*61*) has described a new procedure for determining the boiling point of a pure organic liquid requiring only 2 or 5 cu. mm. The apparatus, which consists of a capillary tube and a liquid heating bath of conventional design, can be operated at either normal or reduced pressures.

VAPOR PRESSURE

Natelson and Zuckerman (*166*) have described a simple method for determining the vapor pressure of one drop of pure liquid with an apparatus made of materials normally in the laboratory. The method is based on the principle that when a drop is partly taken up in a capillary, with some of the liquid remaining suspended from the end, and the pressure is reduced simultaneously at both ends, the meniscus in the capillary descends rapidly when the vapor pressure of the liquid is reached. Reproducibility within 0.5 mm. of mercury can easily be obtained. It is applicable only to pure liquids or pure low melting solids. Gould, Holzman, and Niemann (*73*) have described a method for determining vapor pressure and heat of vaporization of organic liquids on a milligram scale. The procedure is a modification of the Emich method for determining boiling point.

MOLECULAR WEIGHT

Csokan (*46*) has improved the methods of Rast (*187*) and Pirsch (*179*) for determining molecular weight of organic substances. The apparatus consists of a heated metal cylinder containing a capillary tube in which the substance is melted. The tube is so illuminated that the melting can be observed with a lens. The temperature of the capillary is measured by a sensitive galvanometer connected to a thermoelement. Ketchum (*114*) has improved Hallett's modification of the Menzies and Wright procedure for determining molecular weight. The heating coil of the new apparatus is so arranged that it is easily cleaned and the sample container readily recovered. Nash (*163*) has proposed a method based on a vapor pressure comparison method in which lowering the vapor pressure produces a determinate solution of the sample. The measurements are made with isoteniscopes. The weight of sample of nonvolatile compounds can range from 2 to 8 mg., with molecular weights not to exceed 700. The sample can easily be recovered, and the choice of solvent is not limited. Wright (*262*) has described an isothermic distillation method for molecular weight determinations of materials soluble in alcohol. This differs from the more general methods (*168*) of measuring change in volume by measuring change in weight. The alcoholic solutions of the known and the unknown are contained on filter paper instead of in tubes. Accuracy within 10% of theoretical values can be expected.

Nash (*164*) in the design of an effusion microapparatus has added another to the long list of methods that can be employed for the determination. The apparatus used in the methods which employ rise of the boiling point, depression of the freezing point, and isothermal distillation, has been reviewed elsewhere (*79*). The Nash apparatus is useful for determining the molecular weight of 0.5 ml. of permanent gas or 0.5 mg. of volatile liquid.

REFRACTIVE INDEX

In addition to the various methods of determining refractive index of organic substances described by Niederl and others, a simple method of obtaining this physical measurement of an organic compound is that of Fischer and Kocher (*57*). A few millimeters of the sample are mixed with powdered glass of known index of refraction. The temperature of the mixture is raised until the liquid and the glass have the same index of refraction (disappearance of the Becke line). The source of light is a sodium vapor lamp. The index of refraction at 20° C. can be computed.

MISCELLANEOUS APPARATUS

The following discussion includes only pieces of microapparatus developed or improved during the past 6 years that have not been dealt with elsewhere in this review.

BURETS AND PIPETS

During the past few years, there has been considerable interest in the development of rapid, accurate, and simple means of measuring liquid volumes. Gorbach (*67*) devised a microburet without a stopcock which consists of a diaphragm pump and capillary tube with a detachable tip. It has a capacity of 0.2 ml. and an accuracy of 0.1 cu. mm. Lundbak (*147*) modified a Krogh pipet by employing a micrometer screw and a ground-glass piston syringe. Rieman (*188*) designed a new type of buret with a mercury valve. The buret operates on a horizontal position, and the tip is bent at right angles. When in operation, the tip dips below the surface of mercury covered with the solution to be titrated. The liquid in the buret is made to flow by raising or lowering the titration vessel. Stock and Fill (*226*) have designed a buret of 1-mm. bore which incorporates a built-in modification of the capillary break method of control of the gravity discharge.

Wyatt (*263*) designed a micrometer-controlled buret, a modification of the micropipet of Rasebury and Heyningen. Levvy (*141*) adapted the Conway microburet for the delivery of volumes up to 2 ml., using a horizontal tube with a bore not exdeeding 3 mm. Winteringham (*259*) described a 1-mm. buret graduated in 0.01 ml., controlled by mercury in a bulb connected to the tube of the buret with a two-way glass stopcock.

An accurate buret capable of delivering up to 5 × 10^{-5} ml. of solution into a drop under a microscope has been described by Lascalzo and Benedetti-Pichler (*134*). The buret is operated by a leveling bulb containing mercury, and the solution titrated is contained in an open capillary. One end of the capillary is connected to a plunger, which is caused to move back and forth in the capillary to mix the solution. The first automatic buret with pressure control was reported by Llager and Sozzi (*145*). The U-shaped buret utilizes both gravity and surface tension to regulate the flow of the standard solution. Because of the small bore of the buret tube (0.2 to 2 mm.), it is possible to use standard solution as strong as 0.5 *N* and obtain values comparable with macromethods. Saunders (*198*) described a new type of buret made in a U with precision-bore tubing. The wide limb forms a 50-ml. buret.

Allan (*4*) has described a buret with mercury and plunger control with a centrifuge tube as titrating vessel. The solution in the vessel is mixed by a thin glass rod attached to the armature of an electric bell unit.

Natelson and Zuckerman (*167*) modified the Rehburg buret by introducing a capillary side tube having a diameter only a fraction of that of the calibrated portion. By using two stopcocks in the buret, the actual volume of standard liquid used from the large tube is measured by filling it to the original mark with solution held in the capillary side tube. Accuracy of 0.5% is possible with only 3 cu. mm. The buret of Benedetti-Pichler was improved by Lacourt, Stoffyn, and Timmermans (*130*) in that the volume of liquid delivered is not measured by indirect means. Shaeffer, Farrington, and Niemann (*204*) have designed a syringe buret suitable for general laboratory work; with this instrument 0.5 ml. can be delivered with a precision of ±0.5%, depending on the uniformity of the diameter of the syringe plunger.

Stock and Fill (*228*) described a simple syringe pipet suitable for mobile liquids like ether. Using a microscope stand and a syringe, Nordmann (*169*) attained high precision in measuring extremely small amounts of liquid. Gorbach (*70*) developed a micropipet for use with the microfilter rod, which is similar in shape but much smaller than the usual bulb micropipet. Because of its narrow tip, it can be connected to the filter rod with rubber tubing. It is filled by suction. Chinoy (*33*) reports a simple pipet for plant fluids. The plant tissue is ground in an upper chamber of the pipet, and the liberated liquid is carried into the fine stem by capillarity. Lazarow (*136*) has described a pipet in which not only is the liquid measured but which serves as a precipitating and centrifuging cell as well.

Lacourt and Timmermans (*131*) have outlined methods of titrimetric standardization of microburets. The delivered 0.1 *N* biiodate from the buret to be calibrated is titrated with 0.01 *N* thiosulfate measured in a 5 ± 0.01 ml. buret. The thiosulfate titer is checked with solid biiodate. The rate of flow in the microburet is kept constant (10 divisions per 40 seconds) to reduce the effect of drainage. This will give a measure of accuracy of 1% of the total buret volume.

Several new distilling microapparatus have been proposed. To cut down the distance from distilling flask to receiver, Tiedcke (*233*) used an "inside receiver." The basic design is suitable for liquids boiling between 60° and 300° C. It is important that the volume of the distilling flask and condenser tube chamber and connections be less than the volume which the sample will occupy when converted to vapor at the boiling point. Duffau (*49*) also uses the flask-within-a-flask design for the microdetermination of furfural formers.

A small glass center tube fractionating column described by Naragon and Lewis (*162*) has a fractionating section surrounded by a silvered vacuum jacket. Above this section is a distributor which distributes half the reflux from the head to the outer tube and half to the center tube.

CAPILLARY TUBES

Ma and Eder (*148*) have described a new weighing capillary for handling liquids in micro- and semimicroanalyses. It uses a simple filling technique. A solid expelling agent is eliminated. The tube is suitable for 2.50 mg. of sample.

A funnel for filling capillaries with solid material is described by Walker (*240*). The size of the tap end of the brass funnel is determined by the bore of the capillary. The powered material is caused to fall into the capillary by rubbing the funnel with a serrated surface such as the side of a pair of tweezers. A wire plunger is used if the capillary clogs.

GAS ANALYSIS APPARATUS

The Microvol of Sanderson (*197*), a device for measuring small volumes of condensable gases in vacuum apparatus, has been applied successfully to analysis of samples of soil atmosphere and should prove useful in gas microanalysis. The entire sample is measured directly, and the pressure-volume products are easily checked.

Kenty and Reuter (*113*) have described in detail a new apparatus originally designed for determining minute quantities of gas impurities occurring in vacuum tubes. The apparatus isolates the gas in a closed vacuum system. The constituents are frozen out, and identified by their condensation points where possible. Hydrogen and carbon monoxide are determined by ignition with oxygen, and the excess oxygen is removed by contact with a hot tungsten filament. Nitrogen is determined by its speed of exhaustion or by the ratio of the thermocouple gage reading to a McLeod gage reading.

A microanalyzer for extremely small gas samples of 0.4 to 1.0 cu. mm., which was used to determine the constituents in gas bubbles formed in animals decompressed to simulate high altitudes, has been described by Berg (*19*). The apparatus is applicable to the determination of carbon dioxide and oxygen. It consists of a 15-cm. (6-inch) capillary thermometer surrounded by a water jacket with an open bell-shaped absorption chamber blown at one end. The absorbent, saturated lithium chloride, is contained in a short piece of rubber tubing closed at one end and provided with a screw clamp.

For the qualitative analysis of gases on the micro scale, Belcher (*13*) reported and compared the Feigl-Krumholz apparatus and Feigl's modification of the Rassler apparatus. By modifying the Feigl-Rassler apparatus, the drop of reagent is prevented from being drawn from the absorber into the body of the apparatus.

For the collection of various atmospheric contaminants, the Engineering Unit, Division of Industrial Hygiene, National Institute of Health (*53*) has described an all-glass midget impinger, similar to the large one. By using standard-taper joints, the parts of the impinger can be changed without regard to the impinger orifice which was necessary in earlier models.

Whiteley (*250*) has designed a modified Van Slyke gas apparatus in which 0.1 ml. of blood can be analyzed for dissolved nitrogen with an accuracy of 0.002% by volume and a limit of sensitivity of 0.0027 microliter or 1.2 × 10^{-10} mole of gas. The apparatus is adaptable to measurement of the relatively insoluble gases, oxygen and carbon monoxide. It is not so desirable for the soluble gases such as carbon dioxide; however, a saturated salt solution and substitution of monobasic phosphate for lactic acid to liberate the gas from carbonate should give reasonable accuracy.

MELTING POINT

Most of the melting point microapparatus described in the past has been the microscope hot stage type which uses a variable temperature metal block with encased thermometer. Hewitt (*89*) uses a shielded and stirred mercury bath instead of the metal block. The sample to be observed is placed on a cover slip which in turn is floated on the heated mercury; the melting of the sample is observed by means of a microscope. The mercury is heated either by a water bath up to 90° C. or by graphite up to 150°. The apparatus should not be used above 150° because of the volatility of the mercury. The method permits the use of small amounts of sample and fairly accurate measurements of the temperature of the solid. The probable accuracy is ±0.1° C.

MANOMETERS

To eliminate the barometric correction necessary with the instruments of Linderstrom-Lang and Boell, Rocher (*190*) has employed the principle of the Cartesian diver. The apparatus is suitable for the study of small quantities of substances that absorb and liberate gases. LeRoy (*139*) has reported a gage which measures pressure changes with an accuracy of 0.01 mm., with a total pressure of 50 mm. or more.

Brow and Schwertz (*25*) report a sensitive two-liquid micromanometer constructed in such a way that the meniscus between the liquids is located in a capillary section. A slight shift in the levels of the wide-end meniscus causes a great shift in the meniscus in the capillary. Young and Taylor (*266*) have designed a micromanometer useful in molecular weight determinations and in the field of mass spectrometry. The apparatus is a vacuum gage operating on the manometric principle; it is usable for pressure ranges of 10^{-1} to 10^{-3} mm. of mercury.

ELECTRON MICROSCOPE

The electron microscope has been little used in organic microchemistry. Gulbransen, Phelps, and Langer (*78*) have suggested its use in connection with the light microscope, and have predicted that it will be used mainly in the study of precipitates undetectable by the light microscope. They have proposed preparation of samples by diffusion of liquid and solids into a thin Parlodion film.

PYCNOMETERS

Houghton (*97*) has described a pycnometer for measuring 0.01 ml. or less of liquid. It is filled by either suction or capillary action.

Lauder (*135*) has published notes on factors which determine the working range of the Gilfillan-Polanyi micropycnometer. The variation of the density with the pressure of the water in which the pycnometer floats and in the body of the float is taken into consideration.

CONDUCTION CELLS

The inherent difficulty with conduction cells in microanalysis when minute amounts of liquid are used is that the electrodes are not sufficiently wetted by the solution. Blake (*20*) has described an apparatus in which the cell is replaced by a conductometric tube fitted with electrodes not in contact with the solution. Current is supplied from a small 1175-kc. radio frequency oscillator. The modified cell or tube is easily cleaned and can be used with colloids or precipitates.

ELECTRODES

A new glass microelectrode for pH determination has been described by Chinoy (*34*). This electrode consists of a vertical thick-walled tube of Corning 0.015 conductivity glass with an eccentrically blown bulb at its base. A cup-shaped conducting membrane 7 mm. deep and approximately 25 microns thick is blown in the upper region of the tube, which is filled with a saturated solution of quinhydrone in *N* hydrochloric acid. Contact is made by a platinum wire extending between a gold-plated terminal at the top of the tube and the liquid. Contact between the solution of unknown pH in the cup and a saturated calomel electrode is made by a potassium chloride bridge. The cell has shown close agreement with the standard glass electrode for a variety of buffer solutions.

West and Amis (*244*) have described a calomel microelectrode that can be used internally with the dropping electrode for polarographic measurements. This gives results for potentials which agree closely with published values.

EXTRACTORS

Hauptmann (*81*) and others have made a simple microextractor by placing the sample in the longer limb of the U-tube, the top of which is funnel-shaped. The U-tube is suspended in a tube of large diameter, the bottom of which is connected to a boiling flask and the top to a condenser.

To prevent losses during extractions with small separatory funnels even when there is a favorable partition coefficient, Wayman and Wright (*243*) have designed continuous liquid-liquid extractors with capacities of 1 to 30 ml. Two extractors were made, one for immiscible solvents lighter than water and the other for solvents heavier than water. An apparatus for extracting organic preparation from an aqueous medium on a microscale has been described by Stock and Fill (*227*). Efficient separation of immiscible liquids permits the use of small volumes of the extracting liquid even when the solution being extracted is large.

A rapid microextractor for lipides with ethyl alcohol has been described by Hsiao (*101*). The apparatus consists of a cold finger extending into the neck of a 100-ml. Kjeldahl flask. A vial with a sintered-glass bottom contains the sample and hangs within another vial beneath the condenser. A micro filter thimble 10 mm. long and 5 mm. in diameter has been described by Bowden (*22*). The thimble, made of Whatman paper and closed at the bottom is placed in a cylindrical funnel and used for filtering small volumes of liquids.

MICROMANIPULATOR

Cailloux (*30*) describes a new micromanipulator composed of two parts—the manipulator proper and the receptor, which holds the tools. This manipulator is operated by a lever and a hydraulic system of pistons and diaphragms. As there is little loss in motion with such a system, the tools can be closely and accurately controlled.

An automatic vacuum microstirrer has been described by Fill and Stock (*56*). The apparatus has a stirrer plunger which rests in a pool of mercury. As vacuum is applied and released, causing the mercury to vibrate, the vibrations are transferred to the plunger rod, which in turn is connected to the vessel containing the material to be stirred.

TITRATION RACKS

As an aid in the titration of numerous samples, Cantino (*31*) has suggested a simple titration rack which holds eight titration (centrifuge) tubes in such a position that the tubes coincide with an aerating device. By moving the reagent bottle and attached buret from one tube to the next, a series of eight determinations can be completed rapidly.

VISCOMETERS

Two types of microviscometers have been described. The one by Weyer (*245*) measures the viscosity of the liquid in terms of the resistance to the torque between two parallel and horizontal disks, one driven and the other stationary. That of Glynn and Grunberg (*65*) measures the time required for the meniscus of the liquid to move under constant pressure from one point to another in a capillary tube placed in a horizontal position. Directions are given for calibrating the tube and for correction to be applied. When systematic variations occurred, they could be traced to thixotropic or anomalous behavior.

REVIEWS AND SPECIAL APPARATUS

The literature on microchemical methods is extensive, and consequently many reviews have been prepared on various specific subjects. Some of them are listed below.

Qualitative analysis (*123*). A comprehensive survey of qualitative methods for the identification of organic substances, including thermal analyses, with a tabulation of 600 substances.

The history (*91*), development (*195*), and advantages of microchemical analysis (*84*).

Microchemical instruction (*256*).

Practical applications, construction, equipment, laboratory management (*155*) and microanalytical laboratories in America (*242*).

Methods and applications (*14*) and techniques (*17*).

Physicochemical methods, viscosity, surface tension, refractive index (*254*), and density (*258*).

Filtration, including centrifuging, siphoning, capillary, filter sticks, and crucibles (*28, 264*).

Apparatus and methods for titrimetric, gasometric, and photometric microanalysis (*21*). Solids purification (*54*) and recrystallization (*45*).

Microchemical quantitative analysis in clinical laboratories, history and current trends (*209*), and tests suitable for pharmaceutical laboratories (*189*).

Biological applications of microanalytical methods (*18, 212*).

Fat and oil analysis, new apparatus (*69*).

Polarographic microanalysis (*222*).

Automatic microchemical organic analysis (*111*).

Microchemistry and its borderline, and the application of x-ray, ultraviolet, visible, and infrared spectrophotometers, and electron microscope to microchemistry (*157*).

Submicroanalysis (*255*).

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INORGANIC GRAVIMETRIC ANALYSIS

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IN RECENT years there has been marked interest in instrumental analysis as compared to volumetric and gravimetric methods. Strong (*314*) states, "The fact that 50% of 1946 analytical papers are on instrumental methods of analysis indicates their future importance—on the other hand it must be admitted that non-instrumental methods probably will be widely used for some time to come."

The practicing analyst will wisely continue to seek analytical methods requiring less personal judgment and skill, and consequently ensuring greater certainty of precise and accurate results. To meet this demand, universities as well as other research institutions are directing their efforts toward the development of instrumental methods. If it is a fact that the quality of a research atmosphere determines or influences the character of methods of training, the sensible teacher must consider the effect of this mechanization upon analytical training at the undergraduate level. The author ventures a prediction that in so far as basic teaching methods are concerned, following the present feverish enthusiasm for automatic recorders, there will be more intelligent realization that sound analytical training in the formative years is best promoted by the classical methods.

The present review is treated in two sections. The first deals with publications involving general procedure incident to a scheme of gravimetric analysis. The second section is concerned with papers more or less confined to determinations of individual elements which by custom and use are grouped in classes such as elements used for light alloys, steel-forming elements, and noble metal elements. The elements comprising each group are recorded graphically in Figure 1 and the review of each group will be found under the heading indicated on the figure. The reader will sympathize with the difficulty of overlapping areas. The primary purpose of this grouping is to expedite locating pertinent and correlated data.

The researches in the field of gravimetric analysis have been confined largely to detailed examinations of older methods and to the application of derivatives of known reagents. No new reagent for any element comparable in specificity to dimethylglyoxime for nickel has been recorded.

GENERAL PROCEDURES

Preparation of Samples. Sandell (*272*) investigated the contamination of silicate samples when crushed in steel mortars and concluded that an appreciable amount of the hardened steel is taken up by the crushed powder. He recommended that the steel should be low in chromium, nickel, and copper, and that the collar of the mortar should not be used. Touhey and Redmond (*331*) also report iron contamination from the crushing of carbide tips in steel mortars.

Some attention has been paid to methods of attack of refractory samples. Wichers, Schlecht, and Gordon (*347*) attacked refractory oxides, silicates, and ceramic materials by heating with hydrochloric acid or hydriodic acid at 300° C. in a sealed tube. Pucci and Maffei (*251*) discussed the efficiency of attack of various ores and alloys by concentrated hydrochloric acid under pressure.

General Methods of Separation. Gilchrist (*115*) has made significant progress in the development of separation of metals by hydrolytic precipitation at controlled acidity. The range of acidity over which quantitative precipitation occurred was expressed in terms of indicators. Bordoni (*41*) also dealt with the formation of insoluble hydroxides at definite acidities, and gave a list of metals with the pH suitable for quantitative precipitation. Progress has been reported in preliminary separation by means of base exchange. Samuelson (*270, 271*) and Runneberg and Samuelson (*264*) recorded the results of an extended investigation of the optimum conditions for efficient selective adsorption by sulfonic acid organalite, Wolfatit KS. In their gravimetric determination of sulfur in pyrite, the adsorption method produced pure barium sulfate. Accurate results were also obtained for potassium in a phosphate fertilizer.

Preparation for Weighing. Termansen (*327*) investigated the phenomena observed when glass vessels were prepared for weighing. He showed that changes in weight were due not to adsorption of water vapor or to variations in atmospheric conditions but to the difference between the temperature of the air within the glass vessel and in the balance case. Belcher (*22*) dealt with the efficiency of desiccants and concluded that keeping crucibles covered and weighing promptly were of greater importance than desiccation. Thiers and Beamish (*328*) obtained maximum precision and accuracy in most cases by the use of a desiccant whose vapor pressure corresponded closely to average atmospheric humidity. Schulek and Boldizar (*283*) disfavored the practice of drying nonhygroscopic substances and recorded the use of driers in balance cases as likely to lead to errors. McNevin (*194*) described a method for absolute calibration of weights and balance for direct precision weighing. Craig (*68*) discussed the factors affecting constancy of analytical weights. Weights which were gold-plated or covered with lacquer were subject to wear; the latter were likely to gain weight on standing. The use of lead in the inner cavity was objectionable.

Filtration. Nagerova (*219*) described a method for the preparation of ash-free filter papers under laboratory conditions. The average ash content of 9- to 11-cm. paper ranged from 0.0004 to 0.0008 gram. Cuching, Prince, and Seiberlich (*70*) prepared chloride-free paper from unbleached sulfite wood pulp by treatment with sodium peroxide and oxalic acid. The ash content was high but could be reduced by heating with phosphoric acid. Tabak (*317*) observed the phenomenon of carbonized rings formed from a drop of water on filter paper and concluded that analytical residues should not be dried on filter paper at temperatures higher than 110° C. Scribner and Wilson (*285*) published methods for the evaluation of analytical filter papers, which included directions for testing retentiveness toward barium sulfate, rate of water flow through the paper, ash content, bursting strength, and stability, and discussed the relationship between stability and such properties as pH, copper number, and "α-cellulose" content. Later (*286*) the same authors arranged limits for these properties as standards for analytical papers. Aleksandrov (*1*) referred to error due to solubility of fritted glass in ammonia solutions. Majer (*195*) examined the efficiency of the Winkler procedure, which involves collection of the precipitate on a cotton filter, followed by drying in a stream of air and weighing. He concluded that the new method was suitable for small quantities of calcium, lead, and sulfate, but with phosphate significant errors resulted.

Automatic Gravimetry and New Aids. Duval (*83*) adapted the Chevenard thermobalance to give photographic records of weights of precipitates. Komlosy (*169*) devised a procedure for wet determination of precipitates by pycnometer methods. Kul'man (*172*) constructed a new apparatus to carry out a complete analysis in one vessel. The apparatus could be used for determination of barium as barium sulfate, chloride as silver chloride, etc. Leland (*183*) described equipment for removing samples of filtrate without interrupting filtration. Capus (*48*) described a new apparatus for the destruction of organic matter with nitric acid and sulfuric acid and the simultaneous collection of volatile products.

General Gravimetric Reagents. Shome (*293*) discussed the faults of cupferron and suggested the application of various derivatives. With one of these derivatives copper was estimated and separated from lead and mercury. Various advantages of other derivatives were pointed out. Merritt and Walker (*207*) discussed the use of 8-hydroxyquinaldine as an analytical reagent. It was more selective than 8-hydroxyquinoline because it did not precipitate aluminum. Directions for the separation of zinc from magnesium and aluminum, and magnesium with aluminum were included. Evans and Higgs (*91*) dealt with cobalticyanide as a precipitant for metal ions. They describe procedures for determining cadmium in "cable making" alloys, silver in lead, iron in aluminum, vanadium in solutions containing aluminum with a view to the subsequent determination of aluminum, etc. Shennan (*292*) used 5-bromo-2-aminobenzoic acid as an analytical reagent. Precipitates were obtained with most of the heavy metals but not with the metals of Column IIA (Periodic Table). Determinations of copper, cobalt, nickel, and zinc were described.

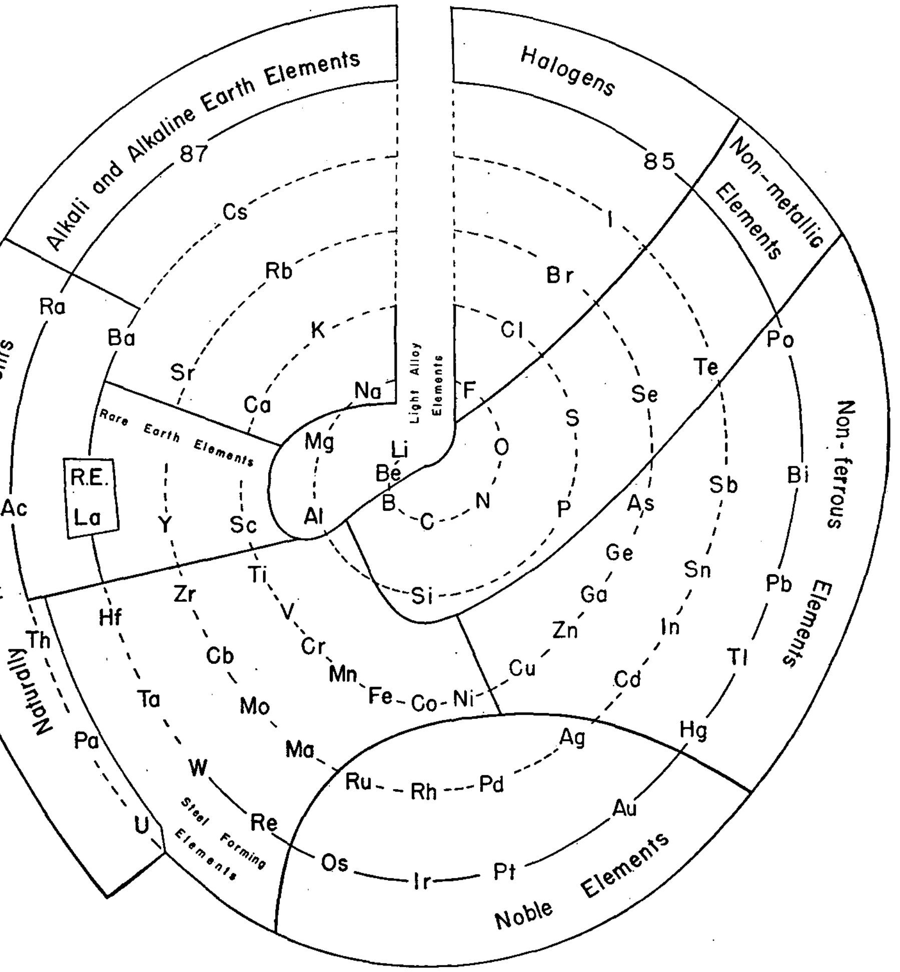

Figure 1. Grouping of Elements for Gravimetric Analysis

LIGHT ALLOY ELEMENTS

LITHIUM

Little that is essentially new in the determination of lithium has been published. Kallman (*161*), dealing with phosphate and silicate minerals, recommended modification of methods based on those devised by J. L. Smith and Berzelius. Most of the interfering elements were removed by calcium hydroxide. Lithium was determined as lithium sulfate after isolation from sodium and potassium by the Willard-Smith *n*-butyl alcohol–hydrogen chloride procedure. Rogers and Caley (*261*) described the isolation from other alkali metals and the precipitation of lithium as a complex periodate and a final estimation by volumetric means.

BERYLLIUM

Sears and Gung (*287*) recommended the use of a mixture of methyl red and bromocresol green as a color indicator for the tannin precipitation of beryllium. They advised an adjustment to pH 6. Ostroumov and Ivanov-Emin (*234*) described the use of α-picoline for beryllium hydroxide precipitation. This reagent forms noninterfering complexes with manganese, cobalt, nickel, and zinc; however, if large proportions of these elements are present a reprecipitation is advisable. Barbosa (*14*) recorded certain sources of error in the precipitation of beryllium by 8-hydroxyquinoline. He examined the precipitate spectrographically, found losses of beryllium through volatilization during ignition, and suggested that this be avoided by the usual preliminary wet oxidation, with subsequent removal of beryllium as the hydroxide and ignition to the oxide.

Stevens and Carron (*313*) investigated the relative efficiency of various methods for determination of beryllium. They reported that the cupferron method of Hill and Lundell was to be preferred; the oxine method yielded low results and the sodium hydroxide method was good, provided tin was absent. In the sodium hydroxide method, the solution was treated with diammonium hydrogen phosphate and excess sodium hydroxide solution. The precipitate was dissolved in hydrochloric acid and beryllium and aluminum phosphates were precipitated; then the aluminum was selectively extracted after a fusion with sodium carbonate. Beryllium was recovered as hydroxide from an ammoniacal solution at pH 6.2. Furnhata (*104*) investigated the action of organic complexing reagents during the precipitation of beryllium and other elements. Precipitation of beryllium hydroxide began at pH 4.14 and was complete at pH 6 to 7. The precipitate dissolved again at pH 10.8. Aluminum hydroxide first appeared at pH 5.69 and was completely precipitated at pH 6.7, dissolving again at pH greater than 13. These precipitates were unstable, changing with time, temperature, concentration, and amount of stirring.

MAGNESIUM

The researches on the gravimetric determination of magnesium were concerned largely with applications to aluminum alloys and with determinations of the relative value of the pyrophosphate and oxine methods.

Gagnon and Shehyn (*105*), dealing with aluminum alloys, found various difficulties with the oxine method; manganese and sodium chloride in amounts greater than 6 mg. per 100 ml. caused interference. Manganese oxinate salted out. Nickel ion also interfered through coprecipitated nickel oxinate, being adsorbed by magnesium oxinate. However, with certain modifications the oxinate method was recommended for aluminum alloys. Gurevich (*133*) determined magnesium in aluminum alloys by selective extraction with sodium hydroxide solution. Aluminum was removed from the residue and after an adjustment of the filtrate to a suitable acidity the magnesium was removed as phosphate and ignited to magnesium pyrophosphate at 1000° C. Koniakovsky (*170*) determined magnesium in aluminum alloys by precipitation of magnesium hydroxide from an alkali cyanide solution, heated to 80° C. Pitts (*245*) recommended treatment of the aluminum alloy with sodium hydroxide solution, dissolving magnesium oxide in aqua regia, and subsequently removing copper and cadmium as sulfides. Magnesium was precipitated from the alkaline tartrate filtrate with oxine. The results were high but contamination with zinc could be avoided by a triple precipitation, or by adding potassium cyanide before oxine. If a small aliquot of the magnesium oxide residue were used a single oxine precipitation gave results favorably comparable to those obtained by the lengthy phosphate procedure.

Bertiaux (*29*) dissolved the light alloys in sodium hydroxide solution, removed lead as dioxide, then added standard magnesium sulfate to ensure at least twice as much magnesium as manganese. Ammonium phosphate reagent precipitated both ammonium-magnesium and ammonium-manganese phosphates, which were subsequently ignited to pyrophosphates. Bressan and Bessazza (*45*) used the phosphate method for the determination of magnesium in light alloys. Manganese and iron were held in solution by addition of ammonium citrate, potassium ferricyanide, and strong ammonium hydroxide. To avoid errors caused by aluminum, nickel, and manganese in the determination of magnesium in aluminum alloys, Bertrand (*33*) introduced slight variations in the standard procedure. Hirschman (*146*) reviewed the analytical methods for aluminum and compounds containing magnesium and recommended the use of 8-hydroxyquinoline for magnesium as a time saver.

In a subcommittee report on the determination of magnesium, Silver, Beshgetoor, and Doushkess (*296*) stated that the results of comparative tests on magnesium sulfate solutions indicated that the phosphate precipitation was more reliable than the oxine method, although the oxine method would find uses in routine work. Goldstein (*120*), working with magnesium sulfate and magnesium citrate, reported that the oxine method was more accurate and advised that the precipitate be dried for 3 hours at 100° to 105° C. rather than for 2 hours. Haynes (*143*) preferred the oxine method in his determinations of bismuth and magnesium. Martin and Green (*203*) recorded that, from a study of four oxine methods for the determination of magnesium, the oxine method using 5% alcoholic solution appeared the most satisfactory. Karunakaran and Neelakantam (*164*), working with minerals, reported that somewhat more manganese was found with magnesium oxinate than with the pyrophosphate procedure. Tournaire (*332*) reported that in the presence of alkali cyanide, contamination of ammonium magnesium phosphate by manganese could be avoided. He also advised against the introduction of sodium and potassium ions.

Evans (*92*) recommended removal of manganese as manganese dioxide with nitric acid and potassium chlorate in the analysis of magnesium, zinc, and calcium ores and products. Steinhauser and Aust (*311*) described a rapid method for determining magnesium as ammonium magnesium phosphate hexahydrate. Jenks (*155*) reported that this hydrate lost considerable ammonia at 85° to 86° C. and all of it at about 700°. At 50° prolonged heating resulted in the loss of about two thirds of the ammonia. The precipitation therefore should be made in the cold and the residue dried below 30° C.

ALUMINUM

The significant contributions deal with the determination of aluminum in alloys. The application to alloys of precipitants such as benzoate, succinate, and cryolite is described.

Stenger, Kramer, and Beshgetoor (*312*) stated that in one operation ammonium benzoate gave a complete separation of aluminum from magnesium and most of the bivalent metals. Various proportions of silica were removed at different stages and the amount of silica retained in the final oxine precipitate was insignificant. Hal'perin (*137*) described the application of the benzoate precipitation to zinc, copper, and aluminum alloys. The precipitate was ignited directly to aluminum oxide. Smales (*298*) used ammonium benzoate to effect a separation of aluminum from cobalt, chromium, nickel, and zinc. The optimum pH was found to be about 4 and the precipitate was ignited to aluminum oxide. In the presence of much nickel or zinc a double precipitation was recommended. Carter (*51*) determined aluminum in zinc-aluminum alloys by precipitating lithium (2 to 5) aluminate from solutions containing ammonium acetate. Zinc was determined in the filtrate by the phosphate method.

Boyle and Musser (*44*) dealt with a basic succinate estimation of aluminum in magnesium alloys. One precipitation only was required for effective separation of the bivalent metals commonly associated in magnesium alloys. The authors claimed this method to be the most rapid and accurate method available. Tananaev and Abilov (*320*) worked on the direct determination of aluminum in alloys containing iron, chromium, titanium, silicon, cobalt, nickel, zinc, and manganese. Aluminum was separated as cryolite, which was determined as such in the presence of cobalt, nickel, zinc, and chromium. If manganese, iron, or titanium were present, the precipitate was not pure cryolite and it was preferable to weigh as aluminum oxide. When it was desirable to reprecipitate the cryolite the residue was dissolved with hydrochloric acid–orthoboric acid.

Various phases of the determination of aluminum in ferrous alloys and products have been investigated. Stumper (*315*) removed iron and manganese as hydrated oxides and used oxine in an ammoniacal acetate tartrate solution. Goto, Kirisawer, and Segawa (*121*) used zinc amalgam instead of hydrogen sulfide to reduce iron and reported improved results. Inaccuracy occurred with more than 50 mg. of chromium. Pigott (*242*) converted iron and alloying elements to ferrocyanides in ammoniacal tartrate solution and used oxine as a precipitant. Steele and Russell (*309*) discussed the difficulties incident to the use of 8-hydroxyquinoline for highly alloyed steels. Raeder and Lyshoel (*252*) stated that iron and titanium could be removed with cupferron in the presence of considerable acid, and subsequently the aluminum determined in a buffered tartrate solution. Hammarberg and Phragman (*139*) dealt with unalloyed and low alloyed steels. Most of the iron and some of the other elements were removed by electrolysis with a mercury cathode. Aluminum was precipitated in the presence of manganese as aluminum phosphate. Ghimicescu and Murea (*113*) also described a method for determining aluminum as phosphate in alloys used in metal armatures.

Bastos (*18*) used a modified phenylhydrazine method on manganese ores for the separation of aluminum from iron and manganese and small quantities of magnesium, calcium, zinc, nickel, cobalt, and copper. The precipitate was contaminated with small quantities of phosphorus, titanium, and zirconium, which were determined separately and aluminum was found by difference. Fogel'son and Kalmykova (*100*) used a mercury cathode and removed manganese as the hydrated oxide, and titanium, vanadium, and iron by cupferron, and precipitated aluminum as the cupferron complex at pH 4 to 5, weighing as aluminum oxide. Box (*43*) precipitated aluminum hydroxide at a pH low enough to prevent major contamination from iron. The chromium was removed from the precipitate as chromate, the iron was changed to ferricyanide ion. Titanium and zirconium were removed with cupferron and finally aluminum was recovered by oxine. Lemoine and Miel (*184*) removed iron, etc., as ferrocyanides, and determined aluminum as oxinate in the presence of potassium cyanide. Kodzu (*168*) preferred to remove iron with hydrogen sulfide in ammoniacal tartrate solution. Goto and Segawa (*122*) determined aluminum in ferrotitanium. They used oxine in an acetate-buffered solution prepared from the aqueous extract of a sodium hydroxide fusion.

Hanus and Sebor (*140*) stated that the dimethylglyoxime-citrate separation of nickel from aluminum proved superior to the basic acetate procedure. Claassen and Visser (*61*) investigated the applicability of oxine for aluminum and titanium separations and determinations. They reported that titanium could be separated from aluminum at pH 5.6 to 6.5 in oxalic acid solution. Liem (*186*) found that Quinsol or Superol compared favorably with 8-hydroxyquinoline as a precipitant for aluminum, copper, and zinc. Marion and Thomas (*200*) published significant data dealing with the effect of diverse anions on the pH of maximum precipitation of aluminum "hydroxide." Oxalate anions raised the pH of maximum precipitation, while such anions as sulfate, and to a lesser degree, lactate, lowered the pH of maximum precipitation. Above a maximum citrate concentration the hydroxide ion was ineffective for the precipitation of aluminum hydroxide. These phenomena were associated with the conception of Werner complexes, the variation in optimum conditions for maximum precipitation of aluminum hydroxide being dependent upon the ability of hydroxyl to replace the coordinated group formed from $Al(H_2O)_6^{+++}$ plus anion. Useful data might be forthcoming from an investigation of the effect of commonly used anions on the efficiency of such precipitants as oxine, and cupferron. Sears and Gung (*287*) recommended a mixed indicator for accurate pH control during the precipitation of aluminum by tannin.

Some work has been reported on the determination of aluminum oxide in aluminum. Murach, Matviev, Shuikin, and Makarovskaya (*217*) used mercuric chloride during the solvent extraction with propyl and butyl alcohol. The residue, suitably treated, yielded aluminum oxide together with a number of insoluble substances. Boner (*40*) dissolved the sample by refluxing with a mixture of aluminum chloride, ammonium chloride, and cupric chloride. Silica was removed from the residue in the usual way.

RARE EARTH ELEMENTS

No new precipitants for the rare earth elements have been reported. However, advances in the analysis for rare earth elements have been made through detailed examinations of known principles. Great progress has been made in the production of pure rare earth elements as the result of the application of amberlite resins to produce adsorption followed by elution with complexing reagents.

Trombe (*334*) improved the control of the hydrolytic separation by using air which had been passed through weak ammonia solution. Moeller and Kremers (*211*) examined the efficiency of the double sulfate precipitation of the cerium group in the presence of the terbium and ytterbium groups. This work was done to supplement previous researches made before complete identification of all members was possible. Beydon (*34*) used radioactive indicators to examine the double sulfate separation of yttrium and lanthanum. The filtrate from the initial precipitation contained 3% of the initial lanthanum concentration. In successive fractions the quantities of yttrium precipitated with the lanthanum represented 16, 4.5, 1.5, and 0.8% of the initial yttrium concentration. When thallium was used instead of potassium to produce a double salt only 2% of the yttrium concentration was found with the lanthanum, but 20% of the lanthanum was found in the filtrate.

Johnson, Quill, and Daniels (*156*) recorded some of the results obtained by various individuals from investigations of the application of amberlite resins for effecting separation of rare earth elements in fission residues. Complexing reagents such as ammonium tartrate and citrate under controlled pH conditions were effective for the extraction from the resins of zirconium, columbium, yttrium, cerium, strontium, barium, iodine, and certain rare earth elements. Kilogram quantities of some of the latter were found to be better than 99.9% pure. With certain rare earth elements 20 to 100 grams of even higher purity were obtained. Spedding, Voight, Gladrow, and Sleight (*302*) separated macroquantities of spectrographically pure rare earths by adsorption on amberlite type resins followed by elution with complexing reagents at controlled acidity. Tompkins, Khym, and Cohn (*330*) also used amberlite resins for the separation of rare earths and other fission-produced radioisotopes.

Dutt (*80*) tested various methods for the separation of rare earth elements from uranium. The oxalate method was found satisfactory up to a UO_3–R_2O_3 ratio of 25. With higher ratios complex oxalate formations caused low results for the rare earths. The use of salicylic acid did not alter the ratio. This ratio was increased to 400 if most of the uranyl nitrate was removed with ether followed by oxalic acid precipitation. The hydroxylamine and hydrofluoric methods were found good but tedious. Barthauer and Pearce (*15*) found that the composition of praseodynium oxide obtained by igniting the oxalate in air at 955° C. was Pr_6O_{11}. Ryabchikov and Terant'eva (*265*) and Marsh (*201*) have published reviews of methods of separation of rare earth elements.

NATURALLY RADIOACTIVE ELEMENTS

THORIUM

Wenger and Duckert (*345*) examined the efficiency of known reagents for the determination and detection of thorium. Out of some 25 reagents four only were recommended: (1) thallous nitrate with ammonium carbonate gave characteristic crystals with thorium or with UO_2^{++}; (2) oxine, which is useful for spot testing of UO_2^{++}, Zr^{++++}, as well as thorium; (3) hydrogen peroxide, with sodium thiosulfate and barium chloride, which reacts with thorium, titanium, vanadium, molybdenum, tungsten, and zirconium; and (4) benzenearsonic acid which reacts with thorium, Ce^{++++}, and Zr^{++++}. Grundmann (*129*) determined thorium in aluminum and some of its alloys. Sodium hydroxide was used for a rough separation of thorium and aluminum, copper was removed as sulfide, and benzenearsonic acid was used to isolate thorium, zirconium, hafnium, and titanium. Thorium was finally determined with oxalic acid. Bohm (*39*) determined thorium in thorium-treated tungsten wires by separating tungsten from thorium with sodium hydroxide and by subsequent precipitation of thorium with oxalate.

Willard and Gordon (*350*) recorded a procedure for determining thorium in monazite sands. The sample was decomposed with perchloric acid, the rare earths and thorium were isolated through the hydrolysis of methyl oxalate in the presence of acid, and subsequently the thorium was separated by the hydrolysis of urea in the presence of formic acid. This method produced a precipitate whose character was an improvement over that generally obtained. Erametsa (*86*) described quinaldic acid as a reagent for thorium. There was no interference from lanthanum, cerium, praseodymium, neodymium, and yttrium. Interference from zirconium was avoided by precipitating in a cold dilute acetic acid solution. There was interference from aluminum, beryllium, chromium, and uranium. Ostroumov and Beruck'yan (*232*) used pyridine at controlled pH to produce thorium hydroxide quantitatively. Sulfate interfered because of the formation of ammonium thorium sulfate. Separation from many bivalent ions could be effected. Ryan, McDonnell, and Beamish (*266*) used ferron in a solution of pH 2 to 3.5 to precipitate thorium in the presence of tungsten, lanthanum, cerium, titanium, nickel, and cobalt. There was interference from silver, mercury, copper, and sulfate ions. Ewing and Banks (*94*) separated thorium from chromium by distillation of chromium dioxydichloride. Thorium was determined finally as oxalate and weighed as thorium dioxide. Justel (*159*), and Moeller, Schweitzer, and Starr (*212*) have published reviews of methods for the determination of thorium.

URANIUM

Hovorka, Sykora, and Vorisek (*149*) discussed the application of β-oxime of isatin to the precipitation of a large group of elements. Uranium was precipitated in the presence of manganese, zinc, cadmium, and magnesium. By a suitable adjustment of conditions interference from barium, strontium, calcium, nickel, and cobalt could be avoided. The uranyl complex was ignited to U_3O_8. The precipitation could be made over the range of 1 to 240 mg. of uranium. The results were a *little high.* Wylie (*357*) discussed the coprecipitation of uranium sulfate and certain rare earth double sulfates. Almost quantitative precipitation could be obtained with certain proportions of uranium and rare earth elements.

ALKALI AND ALKALINE EARTH ELEMENTS

SODIUM

Caley and Rogers (*47*) reported a new reagent for sodium. The older uranyl acetate–bivalent metal procedures were rendered less sensitive to lithium by the choice of cupric acetate and more sensitive to sodium by a suitable alcohol concentration. Veselovskiĭ (*338*) studied the various methods for determining sodium in water and adopted the uranyl–zinc acetate procedure. The results averaged 1.7% higher than the chloroplatinate procedure. He also reviewed various methods of determining sodium. Hale (*136*) discussed the interference of molybdate with the zinc uranyl acetate precipitation. The errors may be positive or negative, and the interference was eliminated by the use of tartaric or citric acids. Ravaglio (*257*) determined sodium in mineral waters with zinc uranyl acetate.

Collins (*65*) discussed the determination of sodium by uranyl acetate reagents. This article should prove invaluable to those interested in the determination of sodium. It represents an attempt to collect, condense, and correlate as much knowledge as possible concerning the subject of determining sodium with uranyl acetate reagents. The subject matter is arranged under 16 headings and there are 187 literature references. Belcher (*23*) reviewed various methods for the determination of sodium, in particular, the precipitation methods involving uranium salts. Some work has been recorded concerning the separation of sodium in specific composite materials. Shchigol (*290*) recorded a new method for the collective separation of sodium and potassium from interfering elements. These are removed by an ammoniacal phosphate solution with subsequent elimination of phosphate by barium chloride, the excess barium chloride being removed by ammonia and ammonium carbonate.

Smart (*299*) has done extensive work on the determination of sodium in aluminum and its alloys. He recorded pertinent data on various methods which required relatively small samples of metal. In one procedure amyl alcohol with mercuric chloride was used to extract sodium, which was determined finally by zinc uranyl acetate. This method was slightly superior to the procedure involving removal of aluminum chloride with gaseous hydrogen chloride, "gassing" with hydrogen sulfide, and treatment of the filtrate to produce the triple acetate. The blank was rather high but the method served well for checking results. A modified Schauer method was also recorded in which the sample was heated to 900° C. and subsequently leached with dilute hydrochloric acid. Aluminum hydroxide was removed and again sodium was determined finally as the triple acetate. This method was suitable only for "pure" aluminum and yielded very low results with most samples.

Williams and Haines (*352*) dealt with the determination of sodium in potassium hydroxide. The aqueous solution was treated with perchloric acid in excess and sodium perchlorate was extracted with isopropanol and determined with a magnesium uranyl acetate reagent containing a relatively high concentration of uranium. The method was rapid and recovery was 94%. Accurate results were obtained by an empirical factor. Cornes (*66*) discussed a simplified procedure for the determination of alkali in silicates. Experience was required for the successful application of the method. Silica was removed by hydrofluoric acid and sulfuric acid and sodium was determined as triple acetate. Marvin and Woolaver (*205*) also dealt with the determination of alkali metals in silicates. Silica was removed by perchloric acid and hydrofluoric acid. The perchlorates were then thermally decomposed, and the ammoniacal leach was treated with oxalate to remove calcium. Oxine was added and after destruction of organic matter and removal of nitric acid the hydrochloric acid solution was evaporated and the alkali metal chlorides were weighed. Kallman (*162*), working with silicates, extended his experiments on lithium extraction by butanol-hydrogen chloride (Willard and Smith reagent) to include the determination of sodium and potassium; upon treatment of the perchlorates in butyl alcohol with this reagent sodium appeared as insoluble chloride and potassium as a mixture of insoluble perchlorate and chloride. Interferences from barium, strontium, and lead were overcome.

POTASSIUM

A few new precipitating reagents have been recorded. Yien and Shing (*358*) suggested the use of zinc cobaltinitrite instead of the sodium salt. Rathsburg and Scheuerer (*256*) described the application of 4,6-dinitrobenzenefuroxan which produced a slightly soluble potassium salt. The cold saturated reagent in 30% alcohol was stable for at least 14 days. Rubidium and cesium were precipitated also but the lithium salt was soluble. The potassium salt and the precipitating media were explosive and should be destroyed. Malatesta (*199*) recorded the fact that sodium or magnesium dimethylpicrate formed insoluble salts with potassium, ammonium, iron, strontium, and barium ions. A separation of potassium from lithium, sodium, magnesium, and calcium could be effected. The range of accuracy was within 1%. De Graaff and Noyons (*124*) stated that the potassium salt of 5-nitrobarbituric acid was sufficiently insoluble to be used for the determination of potassium in the absence of sodium, rubidium, magnesium, ammonium, and barium ions.

Belcher (*24*) assessed the available methods for the determination of potassium. Various procedures for determining potassium in specific materials were described.

CESIUM

Dutt (*79*) determined cesium in the presence of potassium and rubidium by sodium hexanitrolanthanate. The precipitate, whose composition was $Cs_2NaLa(NO_2)_6$, could be weighed directly or the determination could be made volumetrically with acidified cerium sulfate. The method was applicable to mixtures of 25 times as much rubidium and 100 times as much potassium as cesium. The average error was ±0.2%.

CALCIUM

The developments in the gravimetric determination of calcium were largely concerned with its separation from magnesium. Several less known methods in which the calcium was precipitated with anions of the transition elements of Column VI were investigated but the results suggested inferiority to the oxalate methods.

Ievins and Grinsteins (*151*) reported upon the value of the calcium tungstate procedure which dates from 1836. They found that the composition of the precipitate varied with the concentration of the hydroxide ion, and the precipitate held water tenaceously. Rigid adherence to prescribed conditions was necessary and calcium tungstate was too soluble. Contrary to statements in the literature, calcium was not satisfactorily separated from magnesium. These authors also reported on the use of molybdate as a precipitant. Here also the oxalate method was to be preferred although acceptable results could be obtained by molybdate. Separation from magnesium was not perfect and reprecipitation was necessary.

McComas and Rieman (*193*) stated that calcium oxalate monohydrate could be precipitated pure in the presence of Mg^{++}, Al^{+++}, Fe^{+++}, Mn^{++}, HPO_4^{--}, Na^+, and Ti^{++++}. The liquid was buffered at about pH 4.5 and calcium was determined gravimetrically as oxalate, carbonate, or oxide. Ferrey (*96*) reported that the interference of iron in the oxalate method could be avoided by adjustment to pH 4.5 with ammonium citrate. Lassieur (*180*) reported that, at pH 4.5 or higher, over certain ranges of concentration, calcium could be separated from magnesium without reprecipitation if the mixture did not stand too long and that the calcium oxalate could be washed with hot water in spite of its solubility. Chan (*54*) reported on the determination of calcium as oxalate with urea and formic-formate buffer. Schulek and Boldizar (*283*) discussed the difficulty involved in obtaining precipitates as pure substances. They stated that precipitation of calcium oxalate resulted in acceptably pure calcium oxalate.

Vasil'ev and Vegrin (*337*) dealt with the determination of calcium in magnesium alloy. The nitric acid solution of the alloy was evaporated in the presence of oxalic acid crystals, the residue was ignited, and the calcium was extracted with water and subsequently was precipitated as oxalate at pH of about 5 and ignited to calcium oxide. Karaoglanov (*163*) reported that calcium could be separated very nicely from magnesium over certain concentration ratios if considerable excess of oxalate was used and the calcium oxalate was filtered after one hour. While filtering was difficult, there was no appreciable interference from magnesium. However, the excess of ammonium ion could interfere with subsequent determination of magnesium as phosphate. Wright and Delaune (*355*) recommended a large excess of ammonium oxalate to prevent interference of magnesium. They suggested a procedure for determining calcium in magnesite and in brines that contained considerable magnesium chloride. Corrections for the solubility of calcium oxalate in strong oxalate solutions were included. Hazel and Eglof (*144*), in the determination of calcium in magnesite, instead of removing calcium as calcium sulfate, preferred to remove magnesium from a basic mannitol solution. Calcium was determined as the oxalate.

Tananaev and Karabash (*322*) recorded their work on the determination of calcium in magnesium alloys. Magnesium sulfate was selectively extracted by methanol at the "neutrality" of methyl violet. The calcium sulfate was dissolved and the calcium was determined as oxalate. Couturier (*67*) avoided the interference of phosphate in calcium determinations by neutralization with ammonia followed by addition of formic acid. Osborn (*229*) dealt with the determination of calcium in the presence of strontium and barium. The separation was based on the solubility of the sulfates of these three elements in perchloric acid and on subsequent precipitation of barium sulfate and strontium sulfate upon dilution with water. Young and Hall (*361*) determined calcium sulfate in sulfide ores by selective extraction with ammonium chloride, and subsequent precipitation with barium chloride.

BARIUM

The researches on the gravimetric determination of barium were restricted to the precipitation of barium sulfate and barium chromate.

Bogan and Moyer (*38*) described the application of agar-agar to coagulate barium sulfate. Their prediction that by its use much time could be saved in determining small quantities is now accepted generally. Salt (*268*) used picric acid for the same purpose. Schulek and Boldizar (*283*) added further evidence to show that a barium sulfate precipitation did not result in a pure substance. They recommended the factor 1.006, which produced greater accuracy. The suggestion that the error was due to adsorption or occlusion was rejected in favor of coprecipitation of impurities. Schleicher (*276*), referred to a possible source of error caused by difficulty in washing filter paper free from adsorbed barium chloride. This could be avoided by washing the paper with moderately concentrated hydrochloric acid, then hot water before filtration of barium sulfate. Eventov and Patrikiev (*93*) determined the effect of acidity on occlusion of barium chloride by barium sulfate. A large excess of barium chloride was used and it was found that occlusion reached a minimum at pH 3.4.

Pierron (*241*) dealt with the interference of phosphate ion during barium sulfate precipitation. The maximum amount of phosphate was carried down when an excess barium chloride was added suddenly and the contamination occurred as $Ba_3(PO_4)_2(BaSO_4)_n$. The minimum amount was carried down when barium chloride was added slowly at the boiling point and contamination occurred as $BaH_4(PO_4)_2(BaSO_4)_m$. A boiling period preceding filtration reduced the interference. Meldrun, Cadbury, and Bricker (*206*) discussed the coprecipitation of chromate with barium sulfate. In neutral solution barium chromate was nearly as insoluble as barium sulfate. However, under conditions which ought to avoid interference it was found that barium sulfate was contaminated with chromate. Their studies supported the view that solid solutions of barium sulfate and barium chromate were formed. Beyer and Rieman (*35*) dealt with the separation of barium from strontium. The separation by chromate was improved by the use of a boiling solution at a pH of 4.5. With reprecipitation and suitable buffering good results were obtained.

STEEL-FORMING ELEMENTS

TITANIUM

Schoeller and Holness (*279*) described the action of tannin on chloride and oxalate solutions of titanium and associated elements. In oxalic acid solution, titanium was more readily hydrolyzed than was zirconium. In hydrochloric acid solution (below 0.02 *N*) tannin could be used to separate titanium from aluminum, iron, and vanadium, but not from zirconium. With controlled acidity titanium and zirconium could be separated with the aid of tannin from chloride solutions containing aluminum, iron, and vanadium. Traub (*333*) used hexamethylenetetramine to replace hydrogen sulfide for the removal of bivalent iron from titanium with zirconium in certain alloys. With high chromium-nickel steels, tungsten, vanadium, and molybdenum were removed by sodium hydroxide separation. While normally columbium was not completely precipitated, in the presence of titanium and iron the separation was complete.

ZIRCONIUM AND HAFNIUM

Considerable work has been done on the gravimetric determination of zirconium. For the most part, interference from various elements of Column IV and adjacent columns vitiate the procedures. Recently, reagents have been reported for which relatively good specificity is claimed.

Kumins (*173*) reported the discovery that mandelic acid would separate zirconium from the following elements which commonly interfere: titanium, iron, vanadium, aluminum, chromium, thorium, cerium, tin, barium, calcium, copper, bismuth, antimony, and cadmium. The zirconium mandelate was ignited to oxide. Erametsa (*85*) described sodium flavianate as a specific reagent for zirconium. Salts insoluble in water but soluble in acetic acid solutions were produced with lead, mercury, silver, and thallium, but of the ammonium and ammonium sulfide groups only zirconium was precipitated.

Claassen and Visser, and Claassen (*60*, *62*, *63*) reported their investigations of the applicability of phosphates and certain arsenical reagents. The determination of zirconium as $Zr_2P_2O_7$ (*62*) was reported as satisfactory except in the presence of tin and iron. With the reagent *p*-hydroxybenzenearsonic acid (*60*) there was interference from tungsten, tin, and large proportions of titanium. There were also mechanical difficulties with sulfuric acid solutions. Arsenic acid (*63*) would separate zirconium from a large number of elements. Tungsten was coprecipitated and double precipitation was necessary in the presence of bismuth, beryllium, thorium, tin, and titanium. Zirconium was determined finally as zirconium oxide. Ramos (*255*) examined various methods for determining zirconium. The phosphate method was found more suitable than the cupferron method for routine work. Alimarin and Medvedeva (*4*) used benzenearsonic acid for the determination of zirconium in minerals, rocks, and steels. The initial precipitate was ignited, and the residue was fused and treated with tartaric acid and hydrogen sulfide to remove tin and heavy metals. If titanium were present hydrogen peroxide was added. Chernysheva (*57*) determined zirconium in steel as selenite after preliminary precipitation with ammonia in hydrogen peroxide solution. Many of the interfering elements were removed by an aqueous extract on an alkali carbonate fusion. Hoffmann (*147*) determined zirconium in ores with selenium dioxide with final conversion to zirconium dioxide.

Schoeller (*277*) described the selective precipitation of zirconium with tannin. There was interference from titanium and tin. In chloride solution with free acid Zr^{++++} was hydrolyzed readily, but in sulfate solution there was formed a complex zirconyl sulfuric acid which resisted hydrolysis. Fischer and Zumbusch (*97*) separated zirconium and hafnium from aluminum as basic chlorides at 0° C. Recovery was not complete but separation from aluminum, iron, and titanium was effected. Willard and Freund (*349*) used triethyl phosphate in the fractional separation of hafnium from zirconium. If insufficient ester is used 5 or 6 precipitations resulted in a complete separation. Ayres (*11*) suggested a separation of zirconium based on the principle that the hydrated oxide of zirconium, which bears no ionic charge, would not be adsorbed in an ion-exchange column. Amberlite 1R-4 was used.

COLUMBIUM AND TANTALUM

Shchikov and Popova (*291*) determined columbium and tantalum in steel by precipitating and weighing the combined oxides. Tantalum was determined colorimetrically and the columbium obtained by difference. Harpham (*141*) determined tantalum and columbium in tungsten steel by fusion with sodium hydroxide of the insoluble residue from hydrochloric acid treatment, followed by treatment with brine, then with hydrochloric acid solution. Johnston (*158*) determined these elements in stainless steel by standard methods and methods of difference after collectively precipitating tungsten trioxide, columbium trioxide, ferric oxide, tantalum pentoxide, and titanium dioxide with cinchonine solution. Alimarin and Burova (*3*) reported that sodium hypophosphite forms insoluble complexes with tantalum and columbium. In the presence of ammonium oxalate tantalum was separated from columbium as $(Ta_2O_5)H(PO_2H_2)$. Gillis, Eeckhout, and Poma (*116*) stated that ferroin in hydrofluoric acid solution was a useful reagent in the separation of tantalum and columbium. Repeated reprecipitations were necessary.

Oshman (*231*) determined tantalum and columbium in samples of concentrates containing titanium and zirconium. The supernatant liquid from the separatory funnel containing amalgam was treated to precipitate columbium and tantalum along with a little titanium and zirconium. Titanium and zirconium were determined in this precipitate by standard methods and the earth oxides were calculated as a difference. Bagshawe and Elwell (*13*) published a procedure for the determination of columbium in rustless and heat-resisting steels. The steel was treated with hydrochloric and nitric acids, followed by evaporation, baking, extraction with hydrochloric acid, reduction with sulfur dioxide, and filtration. Silica was removed as usual. The residue was fused with potassium carbonate and the hot aqueous extract was treated with a solution of magnesium sulfate, ammonia, and ammonium chloride. The final residue of oxide of columbium, tantalum, and titanium was weighed and the titanium content was determined colorimetrically. Craven (*69*) reported the results of a cooperative examination of this and other methods. He concluded that while four procedures gave satisfactory results, the method of Bagshawe and Elwell (*13*) was the best.

CHROMIUM

Pieri (*240*) determined low percentages of chromium in special steels by precipitation with ammonium hydroxide, followed by an oxidizing fusion and determination as barium chromate. Beguerie (*21*) studied various procedures for the determination of chromium and concluded that precipitation of chromic hydroxide after reduction with ethyl alcohol in acid solution was effective, provided ions such as ferric and aluminum were absent.

MOLYBDENUM

Carlsson (*49*) determined molybdenum in ores, after removal of sodium tungstate from the fused salt, by precipitation with benzoin oxime in a ferrous sulfate–hydrochloric acid medium. Roy and Ghose (*263*) determined molybdenum in high-speed steel by precipitation as sulfide in a tartaric acid medium which dissolved tungsten trioxide and thus prevented the usual adsorption of molybdenum. Carriere and Dautheville (*50*) investigated the effect of acidity on the composition of strontium molybdate precipitates. Strontium molybdate was formed at pH 6 to 8. A lower pH resulted in variable ratios of strontium oxide to molybdenum trioxide. Determinations as strontium molybdate under suitable conditions produced results within 0.5% of the correct values. These authors found that when strontium molybdate was calcined, some insoluble molybdenum trioxide was formed. Directions were given for the determination of strontium content of complex strontium molybdates. Appleton (*8*) suggested the use of Aerosol to lessen the creeping effect encountered during the filtration of ammonium phosphomolybdate.

VANADIUM

Neiricker and Treadwell (*223*) used 8-hydroxyquinoline to determine tungsten, molybdenum, and vanadium with and without the presence of iron. The oxinates of each of these elements were collectively precipitated. Directions were given for the conversion of these complexes to oxides and for the oxinate separation of tungsten and iron, and molybdenum and tungsten. Cass (*52*) published a detailed review of Neiricker's and Treadwell's procedure.

TUNGSTEN

Various aspects of the gravimetric determination of tungsten were discussed in some 22 papers. Lambie (*177*) used tannin with cinchonine to determine tungsten. A procedure was recorded for the determination of phosphorus in the presence of tungsten. Oats (*228*) suggested the use of Rhodamine-B reagent to replace cinchonine. Peterson and Anderson (*238*) compared the cinchonine and tannic acid–antipyrine methods, and a method combining these three reagents. The latter method was to be preferred.

Various reagents have been suggested to replace cinchonine. Platunov and Kirillova (*246*) used β-naphthoquinoline; Gleason (*117*) used nemadine reagent and redissolved with sodium hydroxide instead of ammonium hydroxide. Box (*42*) considered cinchonine a little inferior to Rhodamine-B, although neither reagent effected precipitation of tungsten trioxide. Lambie (*178*) regarded Box's Rhodamine-B procedure as unsuitable for general application and believed that Moser and Blaustein's phenazone (antipyrine) was unreliable. Tananaev and Lotsmanova (*325*) used gelatin instead of cinchonine, and Baumfeld (*19*) described conditions for the precipitation of tungstic acid without the use of cinchonine. Grimaldi and Davidson (*127*) used brucine.

Various authors worked with precipitation as mercury tungstate. Blumenthal (*37*) used mercuric nitrate "reagent" at pH 3.5 and ignited at a maximum temperature of 800° C. Cloke (*64*) determined tungsten trioxide in wolfram, removing tin in both nitric and ammoniacal solution and tungsten with mercurous nitrate from a solution basic to methyl orange. Wirtz (*353*) discussed the precipitation of tungsten with mercurous nitrate in the absence of excess sodium hydroxide, which forms soluble metatungstate. The best results were obtained when tungsten was precipitated with mercuric nitrate. Weiss (*341*) used mercurous nitrate to determine tungsten in minerals. The $Hg_2(NH_2)_2WO_4$ plus mercury was ignited at 750° C. to form tungsten trioxide.

Yoe and Jones (*359*) developed the use of anti-1,5-di(*p*-methoxyphenyl)-5-hydroxyamino-3-oxiimino-1-pentene. Their procedure was applied to alloys and ores with results comparable to those obtained by cinchonine, the purchase of which was subject to restrictions; molybdenum interfered to a degree. De Witte (*354*) stated that the accuracy and simplicity of precipitation as barium tungstate from a neutral solution of sodium tungstate compared favorably with results by cinchonine or mercury salts. Berkem (*28*) expressed the view that precipitation of barium or lead tungstates was to be preferred because these salts were the least soluble and their physical characteristics were an advantage. Evans and Box (*90*) reported a procedure for determining tungsten and other constituents in tungsten carbide tips. Popov (*247*) recorded a method for the quantitative separation of tungsten in nitric acid medium without the addition of alkaloid. Chernikov and Goryushina (*56*) and Ubeda, Gonzales, and de la Sota (*335*) have published reviews of methods for the determination of tungsten.

MANGANESE

Barzaghi (*17*) stated that the precipitation of manganese with potassium peroxysulfate produced a product which varied in composition from the hydrated manganese dioxide accepted in the von Knorre method. Increasing the iron content of the solution resulted in higher values for manganese. Austin (*10*) dealt with the interference of ammonium salts in the precipitation of manganese dioxide. This interference was avoided by the use of $Na_2H_3IO_6$ reagent at pH 4 to 5. After the removal of the ions of the first and second analytical groups, the solution was buffered at 4.4 to 4.8, and the precipitation was made in the presence of formic acid. In the presence of phosphate, retreatment of the filtrate was required. Gusev (*135*) used picrolonic acid to determine manganese in the presence of iron, aluminum, titanium, and chromium. Lund (*189*) found that the analysis of a silicate, after fusion with sodium carbonate following the procedure used for limestone, was characterized by retention of manganese by iron, aluminum, calcium, and magnesium. Manganese appeared in the final filtrate.

RHENIUM

Voight (*340*) described the separation of rhenium heptasulfide from molybdenum by hydrogen sulfide in a basic medium. Geilman and Large (*110*) dealt with precipitation of rhenium sulfide from an acid medium with hydrogen sulfide under pressure. With small quantities of rhenium, coprecipitation with arsenious sulfide was advisable. The rhenium heptasulfide could be converted to rhenium disulfide and weighed as such, or nitron could be used.

IRON

North and Wells (*226*) found that disodium hydrogen phosphate in basic acetate medium at pH 3.5 produced a better separation of iron from cobalt than ammonium hydroxide alone. Davidson (*72*) reported that a boiling solution containing 50% ethanol produced ferric hydroxide which was readily filtered and washed. Anderson (*5*) recorded suitable conditions to ensure complete precipitation of ferric hydroxide and to avoid interference from calcium and reduction to iron on igniting. Ostroumov and Bomshtein (*233*) used pyridine to separate iron, aluminum, and chromium from zinc. Zinc was determined as anthranilate after isolation of zinc sulfide from a solution buffered with sodium acetate and containing chloroacetic acid. Kodzu (*168*) compared various methods of separating iron from aluminum and concluded that hydrogen sulfide in ammoniacal tartrate was to be preferred.

Pinkney, Dick, and Young (*244*) examined the relative degrees of retention of cobalt and sulfate ion when iron was separated by phosphate, ammonium salts, and zinc oxide. With trisodium phosphate a single precipitation left cobalt or sulfate ions in the filtrate. With ammonium hydroxide and ammonium salts, sulfate ion was removed but cobalt was strongly retained; with zinc oxide most of the sulfate and cobalt ions were found in the filtrate and only exact analysis required a second precipitation. Furnhata (*104*) dealt with the interference of oxalic acid, tartaric acid, etc., in the iron hydroxide precipitation. Tananaev and Deichman (*321*) reported a method of separating iron from small proportions of zinc, nickel, cobalt, manganese, cadmium, copper, and titanium which they considered superior to the older methods of hydrolytic precipitation of iron. The separation was based on the formation of the double salts $5NaF.2FeF_3$, $2KF.FeF_3.H_2O$, and $11KF.4FeF_3.12H_2O$. The completeness of separation was dependent upon acidity, etc., and optimum conditions for separation from each of the above elements were discussed.

Majiimdar (*198*) recorded the application of quinoline-8-carboxylic acid which precipitates ferric ion from a solution containing Rochelle salt. The composition of the weighed precipitate was $Fe(C_{19}H_6O_2N)_2H_2O$. Murgulescu and Dragulescu (*218*) determined ferricyanide by precipitation of $[Co(NH_3)_6]$-$[Fe(CN)_6]$ with hexammine cobalt (III) chloride. Castiglioni (*53*) used silver nitrate in an ammoniacal solution to remove ferrocyanide and after acidification with nitric acid determined the ferricyanide as silver ferricyanide. Reviews dealing with the analytical procedure for iron and steel analysis include those of Gaskin (*108*), Klinger (*167*), and Pigott (*243*).

COBALT

Evans (*88*) separated nickel and cobalt from iron by precipitation with potassium hexanitrocobaltate (III) in the presence of orthophosphoric acid, nitric acid, paper pulp, gum arabic, and amyl alcohol. Nickel was separated from cobalt by treatment to form cobalticyanide. Schoeller (*278*) determined small quantities of nickel in a cobalt salt by removing cobalt as cobalt ammonium phosphate in an ammoniacal medium. With small quantities of cobalt in the presence of much nickel, the nickel was removed in a neutral or slightly acidic medium as nickel ammonium phosphate in the presence of potassium peroxysulfate. The soluble chloropentammine cobaltic ion was formed. Cobalt and nickel could be separated from iron advantageously by precipitation of ferric phosphate in a slightly acidic, buffered acetate solution. Young and Hall (*360*) determined cobalt in high-cobalt products by first removing iron as ferric phosphate at pH 3 to 3.5. They rejected ammonium hydroxide precipitation, etc., because of high cobalt adsorption.

Kundert (*174*) used hexamethylenetetramine and triethanolamine to precipitate iron in manganese ores containing cobalt and nickel. Cobalt and nickel were determined by standard methods. Saltykova (*269*) separated cobalt and nickel by precipitation of cobalt as silver hexacyanocobaltate (III). The nickel and cobalt solution was treated with potassium cyanide to form potassium tetracyanonickelate (II) and potassium hexacyanocobaltate (II). Evaporation, followed by treatment with nitric acid and evaporation, again resulted in the formation of potassium hexacyanocobaltate (III) and nickel nitrate. Finally the cobalt was precipitated and weighed as silver hexacyanocobaltate (III). Later Nenakevick and Saltykova (*224*) published essentially the same procedure. Tananaev and Sil'nichenko (*324*) removed iron from cobalt and nickel by crystallization of $Na_5Fe_2F_{11}$. This is essentially the method published in the same year by Tananaev and Deichman (*321*). Lamure (*179*) determined cobalt by treatment with mercuric chloride and ammonium thiocyanate to form $CoHg(CNS)_4$ which was weighed directly. Sharova, Chufarov, and Shnee (*288*) described the optimum conditions for the separation of cobalt and nickel by sodium hypochlorite. Tamayo and Marques (*318*) found that diphenylhydantoin can be used to determine nickel with accuracy equal to the dimethylglyoxime method, and Garudo (*107*) used the thio derivative for the gravimetric determination of cobalt. Various notes have appeared dealing with the explosive nature of the filtrate formed after filtration of potassium cobaltinitrite. Broughton, Laing, and Wentworth (*46*) and de Paiva Netto (*236*) suggested explanations for this phenomenon.

NICKEL

Hanus and Sebor (*140*) found the basic acetate procedure for the separation of aluminum and nickel always imperfect. They preferred the use of dimethylglyoxime in the presence of citrate. Gunev (*132*) stated that anthranilic acid could be used for the precipitation of nickel, zinc, cadmium, copper, and cobalt. Ducret (*76*) separated and determined copper and nickel with salicylaldoxime.

Kirtchik (*166*) reviewed and rejected the older methods for determining nickel in cobalt steels and alloys. The various dimethylglyoxime methods were subject to specific difficulties; the prior nitrite separation of cobalt and the cyanide titration of nickel were also rejected. The recommended method depended upon the formation of potassium hexacyanocobaltate (III) and nickel ion. To accomplish the conversion the author used potassium cyanide which formed potassium hexacyanocobaltate (II) and potassium tetracyanonickelate (II). Hydrogen peroxide formed potassium hexacyanocobaltate (III). The nickel complex was changed to Ni^{++} by addition of formaldehyde. Dimethylglyoxime could then be used to precipitate the nickel. This method is based on principles identical to those underlying the method described earlier by Saltykova (*269*), and Nenakevick and Saltykova (*224*). These authors accomplished the same conversions by evaporation and addition of nitric acid with partial evaporation. However, in Saltykova's procedure cobalt was removed as hexacyanocobaltate (III) and weighed after drying at 130°. Nickel was determined by standard methods. Raithel (*253*) recommended the preparation of dimethylglyoxime reagent by mixing with sodium peroxide and dissolving in water.

Diehl, Henn, and Goodwin (*74*) objected to the use of sodium peroxide because of danger of explosion. This would seem significant because sodium peroxide is used in the Parr bomb procedure for the determination of various constituents in organic compounds. Griffing, De Vries, and Mellon (*126*) examined nickel dimethylglyoxime precipitates spectrographically and found appreciable contamination from aluminum and copper. Aleksandrov (*1*) reported that the filtration of nickel dimethylglyoxime through fritted glass was subject to error owing to the solubility of glass in ammonia solutions. Johnson and Simmons (*157*) used 1,2-cyclohexanedione (Nioxime) as a reagent for nickel. Although the reagent was water-soluble and was a more sensitive reagent for nickel, yet the precipitate did not crystallize well and the results were too high for gravimetric work. Kuras (*175*) used niccolox (oxalenediamidoxime) as a reagent for nickel. Ions such as iron and cobalt which produced insoluble hydroxides with ammonia must be eliminated. The reagent is soluble in water but the results were not so accurate as those obtained with dimethylglyoxime. Chirnside, Cluley, and Proffitt (*58*) used the dimethylglyoxime procedure for determining nickel in nickel-cobalt-iron alloys for glass-to-metal seals. Sulfite was used to reduce iron and the precipitation was made in a buffered tartrate solution. Bertiaux (*32*) began a review to appear in several installments, dealing with the determination in industrial nickel of a large number of elements.

NONFERROUS METALS

COPPER AND CADMIUM

Various new organic precipitants for copper have been developed, some of which offer certain advantages in specific applications. Gilbreath and Haendler (*114*) used 8-quinolinecarboxylic acid in an acetic acid medium. The complex was weighed directly. Separations from cadmium and zinc were effected, but silver and gold interfered. Majiimdar (*198*) described the application of quinoline-8-carboxylic acid (quinaldic acid) to the precipitation of copper, iron, and cadmium. In a slightly acid solution and with Rochelle salt present cadmium was precipitated and separated from copper, arsenic, antimony, and bismuth. Copper could be determined in the presence of cobalt or zinc in much the same way, but Rochelle salt was not added.

Hovorka and Vorisek (*150*) determined copper with isonitroso-3-phenylpyrazolone in either tartrate or acetate medium. Later, these authors extended the use of their reagent. In the presence of ammonium tartrate, coprecipitation of cadmium, aluminum, iron, lead, nickel, cobalt, etc., could be prevented. The organic copper complex was sprinkled with oxalic acid and ignited to copper oxide. Majiimdar (*196*) defended his previous findings on the separation of copper from cadmium with quinaldic acid. For both copper and cadmium determinations, in only 2 cases out of 34 were the errors over 0.1 mg. The solubility of copper quinaldate in acetic acid was shown to be a specific effect and not one due to pH variation. Pritchard and Chirnside (*249*) also obtained satisfactory results in their separation of copper from cadmium with quinaldic acid. Flagg and Vanas (*98*) used quinaldic acid for the determination of copper in cast iron and steels. Reprecipitation at pH 3 was required. Time could be saved if copper were first separated by internal electrolysis. Mukhina (*216*) used quinaldic acid for the determination of copper and zinc in metals. Copper, as the quinaldate, was first removed in an acid medium, the filtrate was treated with Rochelle salt and ammonium chloride, and zinc was precipitated at pH 6.

Several authors worked with salicylaldoxime. Jean (*154*) determined copper in steel with this reagent. At various acidities lead, bismuth, zinc, cadmium, palladium, and cobalt were precipitated. Nickel and vanadium could be partially precipitated. Copper was determined in steel in an ammoniacal acetate medium in the presence of tartrate. If chromium were present the procedure was altered. Ducret (*76*) also worked on the separation and determination of copper and nickel with salicylaldoxime. The effect of pH on the solubility of the precipitate was studied. Duke (*78*) used salicylimine in the determination of copper in brass and bronze. Sarudi (*275*) described additional work on the use of thiosulfate for the separation of copper from cadmium. The impure copper sulfide was ignited to copper oxide, fused with potassium pyrosulfate and subsequently converted to copper sulfide and then to copper oxide. As much as 150 mg. of copper sulfide could be roasted quantitatively. Cadmium could be obtained from the filtrate. Sarudi (*273*) also published the details of a satisfactory procedure for the gravimetric determination of copper as cuprous thiocyanate.

Gunev (*132*) stated that a solution of anthranilic acid could be used for determining copper, cadmium, cobalt, zinc, and nickel. Liem (*186*) used Quinsol or Superol to replace 8-hydroxyquinoline for the determination of copper, aluminum, and zinc. Bertiaux (*31*), dealing with the analysis of copper-lead alloys, published a review of methods suitable for determining copper, lead, tin, nickel, zinc, phosphorus, aluminum, bismuth, manganese, iron, arsenic, antimony, silicon, and sulfur.

CADMIUM

de Wijs (*348*) determined cadmium with ammonium monohydrogen phosphate in neutral solution free from ammonium salts. The precipitate could be weighed as cadmium ammonium phosphate monohydrate or cadmium pyrophosphate.

ZINC

Funk (*103*) used sodium anthranilate to precipitate zinc and cadmium. There was interference from the ions of potassium, sodium, ammonium, nitrate, chloride, sulfate, and acetate. Wenger (*344*) and Gunev (*132*) also worked with this reagent as a precipitant for zinc and cadmium. Ostroumov and Bomshtein (*233*) determined zinc as anthranilate after a pyridine separation from iron in a nearly neutral solution. Zinc sulfide was then precipitated in the filtrate containing $CH_2ClCOOH$ and buffered with sodium acetate. The sulfide was ignited to oxide and finally precipitated as the anthranilate. Separations of zinc from aluminum and chromium were also discussed. Bartram and Kent (*16*) used quinaldic acid to determine zinc in aluminum alloys. With the exception of silicon, the interference from iron, manganese, magnesium, copper, tin, antimony, and lead could be avoided by removal with sodium hydroxide and hydrazine. The zinc complex precipitated over a narrow pH range and the only indicator found to be satisfactory was methyl red with methylene blue (pH 5.2 to 5.6). The pH adjustment should be done in daylight. Gusev (*135*) determined zinc and manganese with picrolonic acid. Iron, aluminum, titanium, and chromium ions did not interfere. Ducret (*77*) found salicylaldoxime useful for the separation of zinc from copper and nickel. These elements separated at pH lower than 7.4 to 8.2, which was the range used for zinc.

MERCURY

Douris (*75*) investigated the action of orthophosphorous acid on mercuric salts in the presence of hydrochloric acid. With considerable hydrochloric acid, a pure white precipitate was obtained which could be weighed directly. Ghaduri and Ray (*112*) used copper biguanide chloride as a reagent for the estimation of mercury in the presence of potassium iodide. The precipitate had the composition $[Cu(C_2N_5H_7)_2]\ HgI_4.H_2O$. Drying at 105° C. removed the water. The method was sensitive to slight variations in conditions. Schroyer and Jackman (*282*) found that dithiane could be used for the quantitative determination of mercury. Copper was found to be adsorbed in appreciable quantities. Chen and Loh (*55*) were able to remove sulfur with hot pyridine from a precipitate of mercury sulfide and sulfur. Krustinsons (*171*) investigated the thermic behavior of mercuric sulfide, arsenious sulfide, and bismuth sulfide. Mercuric sulfide could be heated to about 175° C. Between 194° and 204° C. there was slow transformation to red mercuric sulfide. Beaumont (*20*) published a brief survey of recently developed methods for the detection and determination of mercury.

GALLIUM, INDIUM, AND THALLIUM

Vlodavets (*339*) used cupferron and tannin as precipitants for gallium. Cupferron in the absence of excess ammonia or much ammonium salt was found satisfactory for the separation from indium, beryllium, ferrous iron, and aluminum. The tannin method was also recommended. Titanium and gallium could be separated and determined by tannin. Gastinger (*109*) reported success with the precipitant 5,7-dibromo-8-hydroxyquinoline. Gallium, copper, titanium, vanadium, iron, mercury, and germanium formed stable complexes insoluble in a dilute solution of mineral acids with acetone. Aluminum did not interfere. The gallium precipitate had the composition $Ga(C_9H_4Br_2NO)_3$.

With oxalic acid this complex could be ignited to gallium (III) oxide. Ivanov-Emin and Ostroumov (*153*) recorded the use of pyridine for the precipitation of gallium. The procedure is almost identical to that published for indium (*235*) by the same authors. In the presence of ammonium chloride, gallium hydroxide was separated from the alkaline earth metals by one precipitation. Ato (*9*) described the precipitation of gallium camphorate in the presence of chromium, vanadium, and uranium. The camphorate was ignited and the residue was weighed as gallium oxide. Preliminary to the precipitation, gallium chloride could be extracted with ether.

Babko, Polishchuk, and Volkova (*12*) described the treatment of concentrates for indium determinations. The sulfate solution was treated with gelatin and from the filtrate the more noble metals were removed with cadmium amalgam. Indium, ferric iron, etc., were separated with ammonia, the precipitate was redissolved, and aluminum and iron were removed during treatment with zinc amalgam. Indium was extracted from the amalgam with copper sulfate and finally determined by igniting the hydroxide.

No researches on the gravimetric determination of thallium have been recorded. Chretien and Longi (*59*) reported their critical studies of the 15 gravimetric methods reported during 1902 to 1940 and concluded that only the determination as thallium chromate was worthy to be retained.

GERMANIUM

Weissler (*343*) determined germanium in steel by distillation of the chloride, followed by treatment of the distillate with hydroxylamine hydrochloride and tannin. The precipitate was ignited at a temperature which avoided loss of germanium oxide. Willard and Zuehlke (*351*) stated that germanium was completely precipitated by 5,6-benzoquinoline as a complex oxalate which could be ignited to germanium oxide. Alimarin (*2*) recorded that germanium in coal ash could not be extracted by acids nor isolated completely by distillation. He recommended fusion with sulfur and sodium carbonate. Germanium was finally removed with tannin and ignited to germanium oxide. 8-Hydroxyquinoline was recommended for small quantities of germanium.

TIN

Gray (*125*) used cupferron to determine tin in the presence of antimony. Following oxidation with peroxide, excess ammonia and cupferron effected the precipitation of tin. Gelatin and tannin were added and tin was determined as tin oxide. Mogerman (*213*) used cupferron for the determination of tin in nonferrous metals, following the separation from arsenic and antimony by distillation. Fairchild (*95*) used the mercuric chloride precipitation with direct weighing after drying at 105° C. The solution of the sample was treated with zinc, the sponge was dissolved in hydrochloric acid, and the solution was poured into excess mercuric chloride solution. Wheeler (*346*), in the analysis of steel, separated tin by hydrolysis followed by determination with hydrogen sulfide. Trivalent ions interfered. The method was not applicable to chromium steels.

Mortara (*214*) separated arsenic, antimony, and tin by treatment of the sulfides with sodium carbonate to remove arsenic and subsequently isolated the antimony as $Sb_2O_2S_2$. Tin was determined as sulfide. The method was not recommended for small amounts of antimony. Holness and Schoeller (*148, 280*) extended the use of tannin to the precipitation of tin and its determination in alloys. Separations of tin from tantalum, columbium, vanadium, iron, zirconium, thallium, aluminum, beryllium, and copper were effected with accuracy. Detailed procedures were given for tin determination in white metal with a lead base, brass, bronze, and zinc-base die casting. Price (*248*) published a review of methods used by the Tin Research Institute for white-metal bearing alloys containing more than 80% tin.

LEAD

The researches on the gravimetric determination of lead consist principally of detailed examinations of conventional methods.

Sarudi (*274*) used the chromate method for the separation of lead from copper, cadmium, and iron. Calculations based on the composition $PbCrO_4$ were very satisfactory. However, Grote (*128*) found that under specified conditions a factor of 0.6378 was better than the 0.6411 corresponding to the above formula. The positive error was believed to be caused by adsorption of chromate. The adsorption was found to be proportional to the quantity of lead ion present. With constant proportions of dissolved constituents, the composition of the precipitate was not much affected by rate of precipitation, time of standing before filtration, or extent of drying. Gambrill, Leacock, and Aydelott (*106*) preferred the factor 0.6394.

Sharples (*289*), dealing with lead in graphite-lead-tungsten ores, rejected the molybdate titration method and accepted the gravimetric sulfate procedure. Tungsten was first removed with cinchonine. Bitskei and Kottasj (*36*) recommended fluxing various insoluble lead compounds with sodium hydrogen sulfate and determining lead directly as lead sulfate. Guiva (*131*) applied various methods for the determination of lead in carbon steel. Dissolving the steel in acid with evaporation to fuming of sulfur trioxide and determination as lead sulfate, or removal of lead as lead sulfide with subsequent conversion to lead sulfate, were acceptable procedures. Lassieur and Martelli (*181*) stated that a precipitate of lead sulfate or lead chloride is accompanied by appreciable quantities of antimony. To separate lead and copper from antimony they favored the direct addition of alkali sulfide over the practice of redissolving the antimony from the mixed sulfides. Tananaev and Mizetskaya (*323*) described a method in which lead was removed and weighed as the double sulfate of potassium and lead.

Narui (*220*) dealt with the determination of lead as selenite. Suitable pH ranges were discussed and it was stated that the proportion of water of crystallization in lead selenite dried at 105° C. was influenced by the conditions of precipitation. Anhydrous lead selenite was rarely obtained and was not suitable for the gravimetric determination of lead. Gentry and Sherrington (*111*) precipitated and weighed lead as iodate in the analysis of glasses. Ishibashi and Shimidzu (*152*) examined the relationship between structure of certain organic compounds and their ability to precipitate lead. Acetophenone and benzophenone oximes precipitated lead. The presence of an aromatic radical was suggested as a requirement. They suggested that a mobile hydrogen bound to carbon near the oxime group resulted in the precipitate having 1 mole of oxime to 2 atoms of lead. Shvedov (*294*) used radioactive isotopes of lead to examine the efficiency of separating lead from barium as lead hydroxychloride. Attempts to weigh directly were unsuccessful but a final precipitation as lead chromate was satisfactory.

BISMUTH

Sarudi (*274*) described a modification of the oxychloride method in the separation of bismuth from lead. The low results obtained when the bismuth content was too great were avoided by treating the precipitate of bismuth oxychloride and presumably bismuth trichloride with hydrogen sulfide to form bismuth sulfide. Narui (*222*) accomplished the separation of bismuth from lead by forming either lead sulfate or bismuth oxychloride. Majiimdar (*197*) precipitated bismuth with phenylarsonic acid at pH 5.1 to 5.3. Various anions and cations interfered, but in the presence of potassium cyanide, separation from silver, copper, cadmium, cobalt, nickel, mercury, and lead could be made. The reagent could be used to precipitate zirconium, thorium, and tin under conditions such that bismuth was not precipitated. Stambaugh (*306*) described the determination of bismuth with quinine iodobismuthate and narcotine iodobismuthate. Haynes (*143*) used 8-hydroxyquinoline at pH 5.2 to 5.4 to separate bismuth from magnesium. Gusev (*134*) described a reaction of bismuth with anilino cobalt dimethylglyoxime.

Kakita (*160*) found that potassium iodide and hexamine at pH slightly above 4 formed bismuth oxyiodide which could be dried at 120° to 200° C. and weighed. Krustinsons (*171*) found that bismuth sulfide could be heated up to 120° C. but above this temperature there were oxidation and sublimation of sulfur. Arsenious sulfide could be heated to 120° C., providing the heating was not over 2 hours' duration.

NOBLE METALS

Currah, McBryde, Cruikshank, and Beamish (*71*), during an investigation of the use of thio-organic compounds as precipitants for platinum metals, found that phenylurea, thiophenol, and thiobarbituric acid could be used to precipitate palladium. *s*-Di-*o*-tolylurea and thiophenol were suitable reagents for platinum. Gold could be determined with thiophenol, and rhodium with thiobarbituric acid. Gol'braikh (*119*) found that the dimethylglyoxime method served to determine small quantities of palladium in the presence of considerable nickel. Protopopescu (*250*) reported a procedure for determining palladium and gold in a silver alloy. The details are, in general, conventional.

Belonogov (*26*) investigated the solubility of ammonium hexachloroplatinate in ammonium salt solutions. It was found advisable to precipitate ammonium hexachloroplatinate in a slightly acid solution, saturated with ammonium chloride. The precipitates were reduced with formic acid in the presence of sodium formate. Ramos (*254*) recommended a procedure for the qualitative separation of the platinum metals involving solvent extraction with amyl alcohol. Mukhachev (*215*) used a "wet method" for determining total platinum metals. The ore extract was treated with copper wire from which the platinum metals were removed and determined.

SILVER AND GOLD

Anisimov (*6*) recommended a wet method for the determination of silver and gold in sulfide ores. The ore was treated with sulfuric acid, roasted, and extracted with sulfuric acid. Silver was removed with potassium chloride. The author concluded that the losses of silver and gold were smaller than with the "dry assay" and in the end time was saved. Narui (*221*) published various papers on the analytical chemistry of the selenites. Silver selenite was precipitated in the pH range of 4.3 to 10.2 and separation from magnesium, calcium, and barium could be effected. It could be weighed directly, or the silver determined iodometrically. Stathis (*307*) determined silver with ascorbic acid.

Sollazzo (*300*) determined gold in auriferous samples by repeated extraction with alkali cyanide. The extraction period was reduced by using hydrogen peroxide as an oxidizing agent in the cyanide solution. Erametsa (*84*) used sodium chlorite to precipitate gold. The platinum metals were not precipitated. Stathis and Gatos (*308*) used ascorbic acid. Scott (*284*) assayed solutions for gold by using an aluminum plate in hydrochloric acid solution with lead acetate. The gold was collected in the lead sponge and subsequently treated by fire assay.

NONMETALLIC ELEMENTS

CARBON

Some small variations in the standard combustion methods for carbon have been introduced. Long (*188*) in the determination of carbon in alloys, added tin filings to the charge and burned at 1100° C. in a rapid stream of oxygen. Martin (*202*) stated that activated carbon is a suitable reagent for the separation of silicon tetrafluoride and carbon dioxide. Miranda (*210*) described a rapid determination of carbon in pyrite. Manganese dioxide was used to remove sulfur trioxide from the gaseous solution formed on ignition. Belcher (*25*) used manganese dioxide and silver permanganate as a dry absorbent for sulfur dioxide in the determination of carbon in steels. Touhey and Redmond (*331*), in the analysis of cemented carbide compositions, determined total carbon by combustion at 1000° C. and free carbon by treatment of the sample with nitric acid and hydrofluoric acid; then with phosphoric acid and boric acid, subsequently filtering, drying, and burning. Detailed procedures are given for the determination of other constituents.

SILICON

Developments in the field of gravimetric analysis for silicon deal largely with variations in treatment of samples and the introduction of gelatin to avoid in some cases the customary dehydration procedures. Duval (*82*) discussed the application to analysis for silica of insoluble complexes with silicomolybdic acid combined with bases such as hexamethylenetetramine. The precipitate corresponded to $(C_6H_{12}N_4)_4H_8[Si(Mo_2O_7)_6].4H_2O$. Methods of analysis involving the use of this complex were described. In one method the precipitate was washed with suitable liquids and calcined below 650° C. to produce SiO_2-$12MoO_3$. In a second method the complex was collected in a filtering crucible and dried at 80° C. to produce $SiO_2(MoO_3)_{12}$-$(C_6H_{12}N_4)_4$. Later (*81*) the author published the same procedures for a gravimetric semimicro determination.

The determination of silicon in aluminum alloys was discussed in four papers. Tassieur's (*326*) procedure varied little from the usual triacid attack. For alloys high in silicon he suggested the alkali-carbonate fusion. Osborn and Clark (*230*) used a triacid mix which included phosphoric acid. The optimum dehydration condition was determined by the addition of cobalt nitrate. Bertiaux (*30*) used a nitric-sulfuric acid mix as a solvent followed by dilution with water and addition of hydrochloric acid; filter paper pulp was used as an aid to filtration. Lisan and Katz (*187*) used a phosphoric acid triacid mix, and applied to the solution of the light alloys the coagulating effect of gelatin introduced by Weiss and Sieger (*342*). The method was said to be better than the standard A.S.T.M. method for silicon in aluminum. Norivitz (*225*) in the interests of greater accuracy, suggested some alterations in the Lisan-Katz method.

The determination of silicon in iron and its alloys was discussed in various publications. The Silicon Iron Advisory Panel (*295*) dealt with methods for the determination of silicon in acid-resisting high-silicon irons. They recommended the attack by ammonium chloride and concentrated hydrochloric acid saturated with bromine, followed by evaporation and digestion with concentrated hydrochloric acid.

Fogel'son and Kazachkova (*101*) used gelatin as a coagulating reagent. With malleable cast iron containing less than 18% silicon, the results were lower by 0.05 to 0.08% than with the sulfuric acid dehydration, but the time of analysis was reduced. These findings corresponded to those of Hiigi (*145*), who stated that in the determination of silicic acid in silicates the gelatin method was quicker but the results were somewhat low. On the other hand, Hammarberg (*138*) stated that in the experiments carried out at the Swedish Metallographic Institute on silicon in pig iron, steel, certain ferroalloys, and silicates, the gelatin method yielded results as accurate as those obtained by the conventional dehydration method. Spronk (*305*) also used gelatin with success in a rapid determination of silica in ignited and raw silicates. Khrizman (*165*) incorporated gelatin in his procedure for the determination of silicic acid in carbonate and manganese ores. Tananaev (*319*) used joiner's glue as a coagulant for silicic acid in the analysis of blast furnace slags, and of silicon in cast iron. Guiva (*130*) recorded the application of a specially prepared gelatin filter to the determination of silicon in steel and pig iron. The hydrochloric acid solution of the sample was evaporated to a sirupy liquid, diluted, filtered and the residue, after suitable washing, was ignited and weighed.

Some work has been done on the gravimetric determination of silica in ores. Hawes (*142*) used a dry attack with sodium carbonate and zinc oxide at 950° C. followed by treatment with a triacid mixture containing perchloric acid. Extraction of soluble material was made with ammonium chloride. Philipp (*239*), working with titanium ores, compared various methods of extraction of silica after fusion with potassium pyrosulfate. A simple aqueous treatment followed by the usual volatilization was applicable to small quantities where the best accuracy was not required. Dilute sulfuric acid, in general, had less dissolving action on silicon dioxide than hydrochloric acid.

Steger (*310*) published a review on the determination of free silicic acid in which special attention was given to attack of the sample with hexafluosilicic acid, tetrafluometaboric acid, and orthophosphoric acid. Florentin and Heros (*99*) in their determination of quartz in silicates preferred a double fusion with potassium hydrogen sulfate, with hydrochloric acid washing because it rendered colloidal silica entirely soluble and the quartz remained on the filtering medium. Vasil'ev and Sudilovskaya (*336*) determined silica in fluorides, by fusion with orthoboric acid, fuming with sulfuric acid, filtering, igniting, and weighing silicon dioxide. For contents up to 5% of silicon dioxide, this procedure could be used because the error due to adsorption of boric acid by silicic acid was within the accuracy of gravimetric determination of silica. For 5 to 10% content, a correction must be used. The author used sulfuric acid for dehydration, although Schrenk and Ode (*281*) reported their preference for perchloric acid because calcium perchlorate was more easily removed than the less soluble calcium sulfate. Furthermore in their determination of silica in the presence of fluorspar, they recorded data which indicated acceptable accuracy with samples of calcium fluoride containing more than 10% silica. Lundgren and Thorn (*190*) published a procedure for the determination of silica in magnesium trisilicate.

PHOSPHORUS

Lederle (*182*) found that ammonium magnesium phosphate hexahydrate washed with ammonia and acetone and dried in a vacuum desiccator lost water. An empirical factor was used. Lustig (*191*) recommended calcination of the ammonium magnesium phosphate to burn the filter paper, followed by a wet treatment with perchloric acid and nitric acid. Careful ignition to magnesium pyrophosphate was finally made. Spengler (*304*) dealt with the variation in the composition of the phosphomolybdate precipitate which could be avoided by a sufficiently reduced pressure during washing. While duration of precipitation was not very critical, washing conditions with ammonium nitrate and acetone were critical. Ethyl alcohol and methyl carbonate became attached to the molecule. Detailed conditions for a satisfactory determination were given. Nydahl (*227*) discussed in detail the chemical composition of the phosphomolybdate precipitate and optimum conditions for assuring the normal composition. Strong ignition formed $P_2O_5.24MoO_3$.

Thistlethwaite (*329*) analyzed the ammonium phosphomolybdate, dried at 130° to 150°, and found that the composition corresponded to $(NH_4)_3PO_4.12MoO_3$. However, base-exchange occurred during washing with dilute solutions. Appleton (*8*) suggested the addition of a 10% solution of aerosol to the final potassium nitrate wash to lessen the usual creeping effect experienced during the phosphomolybdate filtration. Fortune (*102*) determined phosphorus in pig iron by precipitation of phosphomolybdate followed by dissolving, and conversion to lead molybdate. Etheridge and Higgs (*87*) used the phosphomolybdate method for the determination of phosphorus in steel containing titanium and arsenic, the effects of which are also discussed.

Speight *et al.* (*303*) dealt with chromium-nickel steels. The procedure involved elimination of arsenic and tin by treatment with hydrobromic acid; the use of strong nitric acid to prevent the inhibiting effects of titanium and vanadium and to prevent formation of soluble zirconium phosphate; and recovery in the presence of tungsten, columbium, and zirconium as ammonium magnesium phosphate coprecipitated with arsenate. Stumper and Mettelock (*316*) recorded the recovery of phosphates as zirconium (2 to 1) and (1 to 1) phosphates. A solution of zirconium oxychloride octahydrate was used, the desiccated residue was treated with hydrochloric acid, and the granular precipitate, after calcination at 1050° C., yielded zirconium (2 to 1) phosphate. Meurice (*208*) recommended differential extraction of phosphorus pentoxide from slags, bones, etc., with a partially neutralized solution of formic acid. Natural phosphates were not dissolved.

SULFUR AND OXYGEN

Researches on the gravimetric determination of sulfur have been confined largely to improvement in methods of coagulation of barium sulfate and studies of interference from iron and chromium. Peskova, Strakhová, and Kushner (*237*) used picric acid along with barium chloride to promote coagulation. Bogan and Moyer (*38*) introduced the much used coagulant agar-agar which reversed the charge on barium sulfate. Goehring and Darge (*118*) removed interference from calcium, iron, and chromium by filtration through synthetic resin (Wolfatit). Samuelson (*270*) found that a sulfonic acid organolite saturated with hydrogen was effective in removing interference from sodium, potassium, calcium, aluminum, iron, or chromium.

Gotto, Kirisawer, and Segawa (*121*) used zinc amalgam to reduce iron and found that the barium sulfate results on sulfur steel were slightly better than with the standard method. Titanium produced inaccuracies but less than 50 mg. of chromium did not interfere. Liang and Li (*185*) stated that the error from chromium in the barium sulfate determination was a negative one and under ordinary conditions was due mainly to complex formation, coprecipitation taking place at higher chromium concentrations. Bepristis (*27*) reduced sexipositive chromium with concentrated hydrochloric acid and ethanol. Wylie (*356*) used ethanol, hydrochloric acid, and glacial acetic acid, obtaining results about 1% low. Evans (*89*) stated that the usual gravimetric determination of sulfur in steel was not noticeably affected by the presence of selenium. Silverman and Goodman (*297*) determined sulfur in bronze and other nonferrous alloys by treatment of the alloy with an aqueous solution of ferric chloride and hydrochloric acid, and subsequently converting the sulfur to sulfate. Millett and McNabb (*209*) found that the chlorides of cadmium, mercury, copper, and arsenic did not interfere with a barium sulfate determination. Under certain conditions copper and cadmium could be removed as sulfides without introducing sulfate ion. This was not possible with bismuth, arsenic, and tin, in which cases the sulfate results were high.

Some work has been done on the determination of various sulfur oxysalts. Dey and Bhattacharya (*73*) treated sodium thiosulfate with silver nitrate, determining the resulting sulfate as barium sulfate and weighing the silver sulfide. Zil'berman and Markova (*362*) determined sulfate in the presence of dithionite and sulfite by treatment with formalin, acetic acid, and glycerol. Romero and Gonzalez (*262*) added calcium chloride to a neutral, alcohol solution of sulfite, bisulfite, and pyrosulfite, producing $CaSO_3.{}^1/_2H_2O$ which was weighed as such.

Gotta (*123*) determined oxygen in steel by allowing aluminum to diffuse into the alloy, resulting in the formation of aluminum oxide. Thus the errors incident to melting were avoided.

SELENIUM AND TELLURIUM

Ripan (*258*) separated selenic acid from sulfuric acid by precipitation of silver selenate in the presence of sodium acetate and acetone at pH of 6 to 7. Ripan and Nebert (*260*) separated these acids by reduction to selenium with hydriodic acid in a current of carbon dioxide. Narui (*221*) found that silver selenite separated from solution at pH 4.3 to 10.2 and lead selenite at pH 4 to 7. Ripan and Macaromaine (*259*) determined tellurium by reduction with hydriodic acid to form elementary tellurium. A rather large correction factor was used. Macarovici (*192*) determined tellurium by treatment with ethanol in a solution buffered with acetic acid or potassium phthalate. The results tended to be low. Selenium did not interfere.

HALOGENS

FLUORINE AND CHLORINE

Specht and Hornig (*301*) determined fluorine in aluminum fluoride as lead chlorofluoride. The aluminum fluoride together with quartz and potassium sodium carbonate was fused at a temperature low enough to avoid the formation of sodium hydroxide and the resulting cryolite. The aqueous extract was treated with lead acetate to form lead chlorofluoride in which the chlorine was determined by silver nitrate. Mart'yanova (*204*) determined fluorine in a chromium bath. The chromate was removed as silver chromate, silver ion was removed from the filtrate, and fluoride was determined as lead chlorofluoride. Ryss (*267*) determined fluorine in tetrafluoborates by adding excess calcium chloride to produce calcium fluoride in the presence of potassium vanadate as a catalyst. The hydrogen ion must be neutralized.

d'Ans and Hofer (*7*) determined chlorine in the presence of large amounts of bromide by the formation of bromine with potassium bromate and aluminum nitrate. Chloride ion was determined with mercurous nitrate. The method could be used with iodides. Lafferty and Varadachar (*176*) estimated total chlorine in bleaching powder by fusion with sodium carbonate. There was no loss of chlorine.

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ORGANIC GRAVIMETRIC ANALYSIS

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DEVELOPMENTS in the field of carbon and hydrogen analysis are considered together in this review, as these elements are usually determined together. A survey of publications on the subject for the preceding 5-year period reveals a constant search for improvement in the chemistry of combustion, and an increasing degree of automatic control and instrumentation, designed to standardize conditions in the conventional combustion procedures, and permitting use of relatively unskilled personnel in determinations formerly calling for a high degree of skill and experience. Willits (*47*) discusses developments in microdetermination of carbon and hydrogen in his review of organic microchemistry.

Most workers continue to prefer filled tubes, and numerous modifications in fillings have been reported. The conventional copper oxide–lead chromate filling has been replaced with silver vanadate on small pieces of pumice (*18*). It is claimed that in microcombustions of compounds containing nitrogen and halogen or sulfur in addition, a better decomposition of nitrogen oxides is obtained. Promising results were also obtained with cerium oxide–silver chromate and manganese oxide–silver chromate catalysts. The use of mixed iron–copper oxide catalysts has received some attention; a mixture of copper oxide plus 1% ferric oxide plus 20 parts of white kaolin has been stated to be more active and stable than copper oxide alone (*6*). A mixed copper oxide–iron oxide (1%) catalyst has been used successfully for the determination of gaseous hydrocarbons (*28*). The modified catalyst permits lower oxidation temperatures (700° compared with 900° C. for copper oxide alone), and in its application the method avoids the need for an oxygen supply of accurately known purity, as well as errors from incorrect measurement of oxygen volume or content of the oxygen supply. The explosion hazard is also eliminated. A comparative study, made using the copper oxide wire method, the slow combustion wire method, the platinized silica gel method, and the precipitated copper oxide method, showed that the latter method gives results equal or superior in accuracy and precision to the other three.

A modification of the ter Meulen semimicromethod uses a 50-cm. layer of manganese dioxide, followed by a 9-cm. layer of lead chromate, over which the combustion products are passed at 450° C. (*8*). By this means 1-gram samples of refractory oils have been successfully analyzed.

Use of platinized asbestos, heated to 300° to 400° C., for the selective oxidation of hydrogen in a hydrogen-methane mixture has been reported (*45*), as well as the use of a high-temperature platinum wire for combustion of methane and hydrogen (*44*).

The determination of carbon and hydrogen in an industrial plant is described (*51*) as being considerably simplified by use of an electric furnace for graudal automatic heating of the sample tube.

A unitized dual apparatus for macrocombustions has been described (*43*), in which a maximum control of the combustion operations is sought as a means for improving speed, accuracy, and precision. Microrotameters monitor gas flow rates, furnace temperatures are closely controlled, rubber connections are limited, and oxygen is introduced at two points in the combustion tube. Conventional tube packing and absorption bulbs have been used, and improvement in results is attributed to close control of mechanical factors.

Critical studies of sources of error in the carbon-hydrogen micromethod have considered oxygen purity, combustion tube filling, and combustion time (*7*). On the basis of tests on commercial oxygen it was concluded that a copper oxide preburner cannot safely be omitted from the system unless the oxygen is tested for impurities before use. Platinum gauze is recommended for use in the combustion tube when refractory compounds are being analyzed, and it was found that the lead dioxide could not be replaced by a permanganate absorber, at least in the micromethod. Extension of the vaporization time up to 15 minutes may prove advantageous for oils and tars, as well as for low boiling hydrocarbons. Comparable vaporization times should be used for all analyses in a series to avoid errors resulting from removal of varying amounts of water from the water-lead dioxide equilibrium.

The hygroscopic nature of asbestos and the manner in which it introduces positive errors in hydrogen determinations have been investigated, and data on the attraction and retention of water to and by asbestos at various temperatures are given (*26*).

Special methods have been reported in a few cases. The determination of carbon in organic fluorine compounds is carried out by a procedure in which the sample is burned in the presence of quartz powder, the water and silicon tetrafluoride are absorbed by sulfuric acid and potassium fluoride solution, respectively, and the carbon dioxide is finally absorbed in the usual way (*30*).

A trend toward simplification of the hydrogen determination is reflected in the lamp method as applied to the analysis of hydrocarbons (*14, 15*). The procedure consists of collecting and weighing, in a phosphorus pentoxide absorber, the water formed upon burning several grams of the volatile hydrocarbon in a modified A.S.T.M. D90-41T sulfur lamp. Considerable improvement in accuracy over the conventional combustion method is noted (0.03% against 0.1 to 0.2%), and the method is well suited for use by unskilled operators. An extension of the lamp method to determine carbon as well as hydrogen has been reported (*40*); the incompletely burned carbon gases are passed through a heated combustion tube, and the emergent carbon dioxide and water are absorbed in the usual way. The method has been applied to both aromatic and aliphatic hydrocarbons, and the precision on 1-gram samples is of the order of 0.01%.

Other Elements. Titrimetric methods seem more popular than gravimetric for elements other than carbon and hydrogen. The decomposition and analysis of organic halogen-containing compounds (including fluorine) have been studied by a method using sodium and liquid ammonia in a sealed tube at room temperature (*27*). Fluoride is precipitated from the product mixture as lead chlorofluoride, but the determination is concluded volumetrically by titration of the chloride in the precipitate.

Surface-active agents may be analyzed for organically combined sulfuric anhydride by digestion with nitric and perchloric acids until decomposition is complete, followed by precipitation of barium sulfate (*10*).

ANALYSIS OF PARTICULAR SUBSTANCES

Hydrocarbons. A method has been reported for the determination of small quantities of acetylene in synthetic acetic acid (*24*). The sample is heated in nitrogen and the gases are passed through 60% potassium hydroxide to remove acetaldehyde, then into a reduced ammoniacal copper solution containing hydroxylamine hydrochloride. Cuprous acetylide precipitates, and after washing is analyzed either gravimetrically or volumetrically for copper.

Styrene may be determined gravimetrically by precipitation as the nitrosite, $C_6H_5CH(NO)CH_2NO_2$ (*2*). The reaction is specific for styrene in the presence of phenylacetylene and butadiene dimer, which frequently accompany styrene. Some diolefins react with the nitrogen trioxide used for the precipitation, but the products formed are soluble in cold alcohol and may be separated in this manner from the styrene nitrosite. The method possesses the advantage of being able to determine comparatively low concentrations (up to 10%) of styrene in mixtures.

A method for determining naphthalene in dilute air samples (*25*) involves measurement of weight losses in a naphthalene tube as the air stream is passed alternately over active carbon and naphthalene.

Aldehydes and Ketones. Studies have been carried out on the gravimetric microdetermination of "very small" amounts of aldehydes and ketones by precipitation with 2, 4-dinitrophenylhydrazine (*41*); compounds determined included vanillin, acetophenone, fluorenone, cyclohexanone, menadione, and furfural. The same reagent has been used for the determination of methyl propyl ketone, although recoveries on milligram quantities are not particularly high (*13*).

The Munson-Walker method for determining reducing sugars has been applied to some of the less common sugars (mannose, galactose, xylose, arabinose, fucose, and rhamnose) as well as to sodium glucuronate and glucurone (*48*). New tables for determining these are given. The method has been restudied in connection with the determination of the more common reducing sugars, and slightly modified tables are given (*11*). Additional tables of sugar-copper equivalents have been given for 0 to 10 mg. of glucose, galactose, arabinose, xylose, and lactose, using the Bertrand micromethod (*35*). A comparative study of four such standard methods of reducing sugar analysis has been reported (*1*).

A method has been given for the determination of D-xylose by precipitation of that sugar as the dibenzylidene dimethyl acetal (*3*). A critical study of the method has been made (*49*), in which conditions necessary to obtain 82 to 100% recovery are established. The precipitation requires 7 days for completion; during the last 24 hours the temperature must be held at 4° C. D-Galacturone and D-galacturonic acid do not interfere, but L-xylose does.

Acids and Derivatives. The gravimetric determination of phthalic anhydride in alkyd resins has been carried out by saponifying the sample with alcoholic potassium hydroxide at 55° C. Potassium phthalate, with one alcohol of crystallization precipitates from the mixture; the alcoholate is decomposed by heating at 150° to 210° C., and anhydrous potassium phthalate is weighed (*9, 12*). Anhydrous conditions must be maintained, as the precipitate is appreciably water-soluble.

Aconitic acid, $C_3H_3(COOH)_3$, a sugar cane product, and its salts have been determined by decarboxylation of the lead salt in glacial acetic acid-potassium acetate solution (*34*). The effluent carbon dioxide is absorbed in the usual type of train. The method is more rapid than a former ether extraction method; sources of error and interference have been studied, and the method appears capable of yielding satisfactory results.

Precipitation with pyridine has been used for the determination of monochloroacetic acid; other halogenated derivatives react under the same conditions (*33*). An interesting electrodeposition method has been reported for pectic acid and pectins (*46*). These materials are negatively charged colloids, and in the method are deposited on a platinum gauze anode from a cooled solution of the material in water and alcohol. The deposit is washed with alcohol, dried, and weighed.

Amines and Related Compounds. The separation and determination of primary, secondary, and tertiary alkaryl amines by a combination of gravimetric and volumetric methods have been described (*38*). Aniline and its ring-methylated and *N*-methylated homologs are separated into groups of primary, secondary, and tertiary amines by forming the toluenesulfonamides of the primary and secondary amines in cold benzene-pyridine solution. The unreacted tertiary amines are removed by steam distillation, and the combined primary and secondary derivatives are weighed. The toluenesulfonamides are separated by extraction with sodium hydroxide, in which the primary derivative is soluble. Following acid hydrolysis the free amines are titrated. The method offers advantages over the older Hinsburg method in that undesirable side reactions are absent, and all the principal reactions go to completion.

Two somewhat similar methods have been described for determining melamine, $(CN)_3(NH_2)_3$ (*21*, *50*). The test solution is acidified with acetic acid and heated, and melamine is precipitated as the picrate. Melamine picrate may be dried at 105° C. and weighed. The reaction is not specific for melamine, and provision is made for removing guanidine and dicyanodiamine.

The formation of an insoluble dithiocarbamate serves for the gravimetric determination of 1-diethylamino-4-aminopentane (*19*). The precipitate forms in acetone in the presence of carbon disulfide, and is dried in vacuum at room temperature and weighed as the hemihydrate, $C_{10}H_{22}N_2S_2 . {}^1/_2H_2O$.

Sulfur-Containing Compounds. The mercaptan content of mixtures of primary mercaptans (thiols) has been determined by precipitation of silver mercaptides, which are dried and weighed (*23*). A novel feature of the method is the use of an amperometric end point to indicate complete precipitation of the mercaptans as the silver nitrate is added.

Sulfapyridine may be determined as the silver salt by precipitation with excess silver nitrate from weakly acidic solution. The precipitate may be dried at 90° to 105° C. (*20*).

Phenols and Derivatives. For the gravimetric determination of a phenol, the sample is treated with formaldehyde and heated. The polymer that forms (resite) may be filtered, washed, dried at 140° C., and weighed (*22*). It seems that such a method would hardly offer advantages over standard volumetric methods. A rapid gravimetric determination of dinitrophenol has been described wherein the phenol is precipitated from a solution of its sodium salt by means of nitric acid (*31*). The precipitate may be dried at 90° to 100° C. and weighed, or dissolved in excess standard alkali, the remaining portion of which is titrated.

Along somewhat more explosive lines is a method for determining trinitroresorcinol and trinitrotriazidobenzene (*37*). The former compound in solution is treated with a solution of phenylacridine hydrochloride. Upon neutralizing and boiling, a precipitate forms which may be dried at 80° C. for weighing. If one is dealing with lead trinitroresorcinate, the lead is first precipitated with bicarbonate and removed before adding the phenylacridine. Trinitrophloroglucinol is determined in the same way, and as trinitrotriazidobenzene may be converted to that compound by treating with dilute alkali, a means for determining it is also at hand.

Natural Products. A gravimetric method for cholesterol has been described in which the sterol is converted to a sulfonic acid derivative of cholesterilene in chloroform. This compound, finally obtained in a water solution, precipitates upon addition of barium acetate as $Ba(C_{27}H_{43}O_3S)_2$, which is dried and weighed (*29*).

An extraction procedure is reported for determining caffeine in erva-maté; the alkaloid apparently is not obtained in a pure state for final weighing as the results are high (*5*). Nicotine may be determined by precipitation with silicomolybdic acid, said to possess advantages over silicotungstic acid when used for the same purpose (*4*). A preliminary isolation is effected by steam distillation of the alkaloid into hydrochloric acid, from which it is precipitated as $(C_{10}H_{14}N_2)_2 . SiO_3 . 12MoO_3 . H_2O$, dried at 110° to 120° C., and weighed.

Miscellaneous Determinations. The gravimetric determination of phenothiazine has been described, in which the material in alcohol is precipitated with chloroplatinic acid (*32*). The precipitate of $Pt(C_{12}H_9NS)_2Cl_4$ is dried at 100° C. before weighing.

Leptazol (pentamethylene tetrazole) has been determined by precipitation with mercuric chloride and weighing of the mercuric chloride complex (*17*).

The determination of hexamethylene diisocyanate has been carried out by condensing it with aniline, steam-distilling out the excess aniline, and weighing the condensation product (*42*). The method may be used also for benzyl and cyclohexyl isocyanate.

1-Propoxy-2-amino-4-nitrobenzene is a synthetic sweetening agent; it is insoluble in alkali, and may be extracted from aqueous solution with ether, dried, and weighed (*16*). Appropriate modifications of the procedure are given if fat is present in the sample being analyzed.

The analysis of carbowax compounds—solid polyethylene glycols—has been described using the precipitation reaction of these compounds with silicotungstic acid (*36*). The precipitates are ignited before final weighing, and the method is calibrated by use of known samples to obtain the proper gravimetric factor.

Benzidine hydrochloride has been used to precipitate the sodium salt of oleyl methyl tauride (Igepon T) from acid solution (*44*). The precipitate is washed with petroleum ether, dried, and weighed.

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INORGANIC VOLUMETRIC ANALYSIS

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VOLUMETRIC methods as applied to inorganic analysis have seen, in the past several years, the usual modifications and reviews of existing methods, as well as some that are new and novel. Several innovations and improvements of existing apparatus have been made.

Publications describing the results of European workers have been received irregularly. As a result, references are incomplete; however, the work of Russian workers since the end of World War II has been discussed in French (*212*).

TITRATION

Reviews and examinations include a textbook on titration methods (*96*); the precise measurements of volume (*201*); procedures and techniques for colorimetric titrations with photoelectric instruments (*216*); apparatus and techniques for amperometric titrations (*191*); potentiometric titration methods with special attention to microchemical applications (*145, 192*) and to arsenic and iron (*62*); new and existing methods for tungsten (*26, 146*), thorium (*139*), and vanadium (*148*); potassium as cobaltinitrite, chiefly in plant ash (*208*); cobalt in steel by ferricyanide (*8*); the effect of iron in the reduction of molybdate in determining phosphorus (*129*); the Karl Fischer procedure for water (*37, 177*); and the iodometric determination of thionalide as applied to bismuth, mercury, and copper (*101*). A discussion of the strength of acids in various organic solvents is of interest (*224*). A graphic procedure has been advocated as a means of determining the results of volumetric analysis (*207*).

Apparatus and accessories (*142*) for automatic titrations, whereby it is only necessary to prepare and load feed units, have been described (*118*) and are on the market (*157*). The automatic recording of titrations as applied to potentiometric, amperometric, and absorptiometric titration has been made with recording potentiometers (*73*). Further work on the use of high frequency oscillators (*87*), which at one time promised to revolutionize volumetric analysis, has not been found. A simple apparatus, requiring only a battery, a microammeter, a variable resistance, and silver and copper wires for electrodes has been used with good results for the rapid analysis of chloride (*49*). Apparatus for polarization dead-stop end points has been described (*58*) which is essentially that of earlier workers (*65*). A cell suitable for conductivity determination of chloride in sea water is useful as a time-saver (*4*). Titrations have been made using photoelectric colorimeters (*160*) which are a further application of previous work (*149, 217*). Among the several types of burets that have been suggested, are an electrical solenoid-operated buret which avoids stopcocks but may be prone to leak (*145*); a rather complicated microburet, controlled by addition of water to a mercury level (*174*); a syringe microburet (*181*); and a micropipet for titration of microgram samples (*125*). An essentially new technique for operation of a microburet appears useful (*167*). Electronically controlled apparatus for distillation of fluoride or hydrofluosilicic acid (*218*) is an important improvement.

Several variations from the usual run of the mill methods are of interest. Among these are titrations in strongly colored solution by adding a solution of a complementary color (*20*); titration of dark colored solutions by extracting with ether prior to titration (*99*); extracting sulfuric acid from crude sulfonic acids with *n*-amyl alcohol, which is then extracted with water prior to titration (*47*); and titrating fuming sulfuric acid with water at 10° C. (*19*). Aluminum has been determined in pigments by dissolving in ferric sulfate solution followed by permanganate titration (*116*). Free alkali in plating solutions is determined by adding excess barium chloride and alcohol and titrating to a phenolphthalein end point; after filtering, the precipitate is titrated with hydrochloric acid (*184*). Magnesium can be titrated as oxalate after precipitation from 85% acetic acid with ethyl oxalate (*75*).

Luminescent titration under ultraviolet radiation has been used to determine lead with sodium oxalate using fluorescein as an indicator (*92*). The use of photoelectric instruments instead of the eye for determination of end points (*127*), both colorimetric (*127, 136, 161, 217*) and turbidimetric (*43*), has increased in Europe. Use has been made of anionic agents to titrate cationic agents and vice versa with appearance of turbidity at the end point (*102*). The effect of various salts and acids on the iodometric estimation of persulfate and vanadate has been investigated. By adding cuprous iodide, oxalic acid, or ferrous sulfate, reactions are catalyzed to such an extent that iodometric determinations of persulfate and vanadate can be made (*161–164*).

Amperometric titration of dilute chromate solutions (*95*) is another application of the interesting rotating platinum electrode. Determinations of arsenic by coulometric titration by electrically generated bromine using an amperometric end point have been made (*144*). Potentiometric methods have been advocated for beryllium by titrating with sodium fluoride (*199*); selenium and tellurium with chromous ion (*123*); nitric acid in oleum (*128*); phosphate by an indirect method (*63*); and thorium with potassium iodate (*190*). An important study on conditions for potentiometric titration of titanium has been made using a mercury indicating electrode (*119*).

When traces of certain elements are to be determined, the dithizone titration technique has been used for copper (*176*), lead in copper, nickel, and cobalt (*226*), nickel (*227*) and zinc (*225*) in cobalt. Another extraction method extracts iodine with chloroform, adds water, and titrates with thiosulfate in the determination of ferric compounds (*200*).

STANDARD SOLUTIONS AND REAGENTS

The question of standard solutions and reagents for analysis is always of considerable importance. Variations of standardization methods have been examined for iodine (*10*), and for thiosulfate, thiocyanate, and permanganate solutions (*211*). Molybdenum (V) as a volumetric reagent shows considerable promise (*203*). Methods of storing and dispensing oxygen-sensitive solutions (*124, 193, 205*) and the use of chromous solutions have been critically examined (*119, 123, 206*). The direct titration of acidified arsenic solutions with dichromate has been stated to give high results (*156*). Five leading brands of reagent grade sodium carbonate were found to have purity satisfactory for a standard reference (*31*). The use of sulfamic acid as an acidimetric standard has increased. Ferrous ethylenediamine sulfate shows promise as an oxidimetric standard (*29*). The following reagents are of interest: metallic silver as a fundamental standard in acidimetry (*68*); substitutes (*143*); mercurous perchlorate for iron (*158*); phosphate (*98*) and ammonium vanadate (*207*) for many elements; chloramine-T for tin (*48*); 8-hydroxyquinaldine in place of 8-hydroxyquinone (*135*); potassium chlorostannate for vanadium and molybdenum (*88*); ferrocyanide as a reducing agent (*186*); naphthyloxychlorophosphine for water (*117*); and iminodiacetic acid for hardness of water (*179*). The use of starch to prevent precipitation of thorium fluoride in the titration of fluoride has been advocated (*194*). The preparation of silver for use in the silver reductor has been described (*187*).

INDICATORS

Several new indicators have been suggested and the usual variations of the old ones have appeared. Solochrome Brilliant Blue has been used with thorium in the estimation of fluoride (*138*). A sodium salt of starch glycolic acid (*151*) and amylose (*115*) appear to be more useful than the usual starch solution in iodometric analysis. Suggested for argentometric titrations have been *p*-dimethylaminobenzylidenerhodanine (*76*), resorcinolsuccinein (*133*), phenolphthalein (*131*), and mercurous ion and diphenylcarbazone (*70*). Indicators of special interest are 2, 2′-bipyridine ferrous complex ion, which is less expensive than other reagents of this group (*28*), derivatives of diphenylaminesulfonic acid for titrating arsenite in alkaline solutions (*217*), phenylanthranilic acid in the method whereby Mo (VI) is reduced to Mo (V) (*64*); diphenylcarbazone for zinc and nickel (*55, 57*); and eriochromeschwarz in the "complexometric" titration of alkaline salts (*15*).

Other workers have used cochineal with hypochlorite (*17*); 1-naphthol for iron (*1*); and cacotheline for calcium and iron (*91*). The acidimetric titration indicators suggested are modified methyl orange for direct titration of sodium carbonate (*30*), disulfonates for alkalinity of water (*198*), and emodin for weak acids and bases (*210*). Cellosolve has been advocated as a solvent for phenolphthalein, as it does not evaporate like ethyl alcohol (*84*).

ANALYSIS OF ELEMENTS

In methods as applied to individual elements there are some innovations, as well as application of time-worn methods:

Aluminum. Determined in aluminum pigments by dissolving in ferric ion solution and titrating ferrous ion formed (*149*); fluoride titration with ferrous ion and thiocyanate as indicator (*168*) or in neutralized tartrate solution (*189*); a rather complicated procedure based on fluoride complex formation (*79*); oxine with bromometric estimation in titanium pigments (*9*); acidimetric titration of aluminate ion with hydrochloric acid using a potentiometric end point (*27*), as well as a basic titration using alkali and a glass electrode (*100*).

Antimony. Separation by volatilization followed by the usual bromate titration (*85, 107*).

Arsenic. Coulometric titration (*144*); with cerate ion in perchloric acid (*188*); iodometrically on arsenic trioxide in arsenic (*103*), on the chloride after separation by volatilization (*150*), on arsenic ions after coprecipitation with magnesium ammonium phosphate (*93*), and after precipitation of elemental arsenic by hypophosphorous acid (*66*); hypobromite titration of arsenite in alkaline solution, with the new diphenylamine sulfonic acid indicators (*217*); and a simplified bromate method (*85*). In the presence of catalysts such as rhenium, arsenate is reduced with stannous chloride in the presence of tartaric acid before iodometric titration (*204*).

Barium. Amperometric titration of chromate in ethanol solution (*94*); phosphate titration (*98*); and ignition of carboxylic acid salts to carbonate followed by addition of hydrochloric acid (*183*).

Beryllium. Potentiometric titration with sodium fluoride (*199*).

Cadmium. Determined potentiometrically with alkali (*33*), and by a rather involved silver sulfide method (*105*).

Calcium. Modifications of existing oxalate-permanganate methods (*72, 120*). A method employing cacotheline as indicator appears to be satisfactory (*91*).

Cerium. *N*-phenylanthranilic acid is recommended as indicator (*40*).

Chromium. Electrometric titration involving the Pt/H_3PO_4/Hg_2HPO_4/Hg electrode gives excellent results in steel (*16*). Perchloric acid oxidation for thorium-chromium mixtures (*59*); an apparatus for retaining chromyl chloride when using perchloric acid oxidation (*178*); and variations in time-honored methods (*14, 18, 52, 147, 170, 171, 202*).

Cobalt. Cyanide and ferricyanide methods are examined critically (*8, 87*). Ferricyanide titration in alloys (*44, 80*).

Columbium. In complex salts by alkalimetric titration (*35*); reduction in Jones reductor followed by permanganate titration (*67*).

Copper. Extractive titration with dithizone (*176*); determination of cuprous ion by titrating with permanganate, dichromate, or ceric sulfate (*83*); a new method whereby cuprous thiocyanate is precipitated after reduction with sulfur dioxide, dissolved in ferric alum, and the ferrous ion formed is titrated (*24*).

Fluorine. Titration with alumium chloride using Eriochromcyanine R as an indicator (*175*); modifications of existing methods using alizarin sulfonate (*90, 221*) or Solochrome Brilliant Blue (*138*). Starch has been used to prevent the formation of thorium tetrafluoride in the titration with thorium nitrate (*194*).

Germanium. Hypophosphite is used to reduce $GeCl_4$ to $GeCl_2$ followed by iodometric titration (*86*).

Gold. Reduction with standard ferrous ion followed by permanganate (*209*); instead of weighing after formaldehyde reduction, dissolving in standard iodide and back-titrating with thiosulfate (*113*).

Halides and Halates. Determination of hydrochloric acid in presence of chlorine by boiling to remove chlorine and titrating hydrochloric acid with alkali (*12*); chloride by amperometric method (*81*), conductometric (*4*), and potentiometric (*49*) titration with indicator by extracting color into ether (*76*), modification of Berg's method (*213*); interesting method by reaction of soluble chlorides with solid mercurous iodate and, after filtering, by iodometric titration of precipitate with thiosulfate (*7*); chloride after adding thiocyanate and ferric nitrate, titrating with mercuric nitrate (*154*); chlorates by titrating with methyl orange solution (*41*), iodometric (*220*), ferrous sulfate reduction (*219*), or Volhard method after bomb reduction (*134*); reaction of hypochlorite with hydrazine sulfate, which is then back-titrated with hypochlorite solution (*36*); chlorate and hypochlorite with sodium benzene sulfinate (*6*); hypochlorite and hypobromite based on selective reduction of hypobromite with alkaline phenol (*60*); iodide by automatic titration (*118*) and by thio sulfate at controlled pH (*5*).

Iron. Ferrous ion determined in presence of thiocyanate by complexing thiocyanate with mercuric nitrate before titration with dichromate or permanganate (*23*). 2, 2′-Bipyridine ferrous complex indicator with cerate titration gives excellent results (*28*). Cacotheline as indicator gives acceptable results by using stannous chloride to titrate ferrous ion (*91*); ferric ion in ferrous lactate and tartrate by liberating iodine in bicarbonate with potassium iodide, extracting with chloroform, and then adding water and titrating with thiosulfate (*200*). Mercurous perchlorate has been suggested as a volumetric reagent but results are not stoichiometric (*158*). Application of the cerate titration to micro amounts has given results as good as colorimetric in the 100- to 500-microgram range (*188*). Automatic titrations have been made using cerate (*118*) and chromous ion (*119*). Applications of existing methods (*67, 171, 207*).

Lead. Luminescent titration with sodium oxalate and fluorescein (*92*); potentiometric titration with alkali fluoride by precipitating chlorofluoride, end point given by drop in ferric-ferrous oxidation reduction potential (*61*); dithizone extraction titration (*226*); as iodate (*38, 71*); and as molybdate (*159*).

Magnesium. Good results are obtained by using the slow decomposition of ethyl oxalate in 85% acetic acid, the oxalate being precipitated in a form suitable for filtration and titration with permanganate (*75*); variations of existing methods by precipitating with standard alkali, filtering, and titrating excess alkali (*222*), adding alkali to pink color of trinitrobenzene and back-titrating with hydrochloric acid to phenolphthalein end point (*45*); in aluminum alloys (*50*).

Manganese. In a new method with few interferences, a neutral manganous pyrophosphate solution is titrated potentiometrically with permanganate to give a pyrophosphate complex (*121*). For solutions brightly colored with nickel, permanganate is titrated with ferrous ion using diphenylamine as indicator (*112*). Titration with phosphate for rough work (*97*).

Mercury. Modification of methods whereby mercurous ion is determined iodometrically and total mercury by cerate oxidation followed by thiocyanate titration (*215*); mercuric oxide by reaction with potassium thiocyanate instead of potassium iodide to form potassium hydroxide, which is titrated (*25*); stannous chloride reduction (*13*); precipitation by iodate and iodometric determination on precipitate after filtration (*39, 69*).

Molybdenum. In a reduction of Mo (VI) to Mo (V) with mercury instead of Mo (III) with zinc amalgam, solutions are not oxidized by air and vanadium does not interfere (*64*). In mixtures with vanadium by sulfur dioxide reduction for vanadium followed by zinc reduction for molybdenum and vanadium (*34*); acidimetric and barium salt titration (*78*); replacement of stannous chloride by K_2SnCl_4 for reduction recommended (*88*); precipitation with 8-hydroxyquinoline followed by usual bromometric titration (*8, 140*).

Nickel. Extraction methods using dithizone titration for small amounts (*227*); extraction into amyl alcohol with diphenylcarbazone followed by cyanide titration (*55*); oxine precipitation followed by iodometric (*141*); cyanide titration in steel (*18, 170*).

Nitrogen. Study of various procedures for nitrogen in refractory metal carbides (*165*); determination of nitrites by adding excess of hypochlorite and back-titrating with potassium iodide (*32*); nitric acid in oleum by electrometric titration (*128*). Nitrates are reduced by ferrous sulfate and silver nitrate in the Kjeldahl method (*46*); nitrates by treating with standard ferrous sulfate followed by back-titrating with dichromate (*108, 111*).

Phosphate. Argentometric potentiometric titration at pH 9 or determination by adding standard silver nitrate at pH 7.5 and back-titrating with potassium bromide (*22, 63*); alkali titration (*110*). Phosphomolybdate precipitate is dissolved in standard alkali and back-titrated with sulfuric acid (*82*); complicated bismuth precipitation finished by iodometric titration (*74*); alum or ferric chloride titration (*153*).

Platinum. Reduction of Pt (IV) to Pt (II) by titrating with standard ferrous ion under carbon dioxide, then titrating excess with ammonium vanadate, using phenylanthranlic acid as indicator. Can be used to determine alkalies (*197*).

Potassium. Determined in sodium-potassium alloys by reacting with absolute alcohol under neohexane followed by titration with standard acid (*214*); cobaltinitrite with permanganate (*104*); a review of cobaltinitrite methods with recommendations of ceric sulfate as titrant (*208*); periodate precipitation followed by arsenite titration (*172*).

Rhodium. Oxidation to Rh (V) with sodium bismuthate and after filtering to remove bismuthate titrating with ferrous ion, using phenylanthranilic acid as indicator. Platinum does not interfere but iridium does (*196*).

Selenium. Potentiometric titration with chromous ion in 9 *N* hydrochloric acid at 60° to 70° C. (*123*), precipitation of silver selenate at pH 7 with standard silver nitrate and after filtering, back-titrating with potassium chloride (*169*); precipitation of selenium followed by iodometric titration (*54, 155*).

Silicon. Precipitation as yellow hexamethylenetetramine silicomolybdate. Precipitate is hydrolyzed in slightly acid solution to give formaldehyde and ammonia, which is treated with standard bisulfite and then back-titrated with iodine (*53*).

Sodium. Variations of acidimetric method (*166, 184*); alkali determined in permanganate by reduction with acid solution of peroxide (*126*).

Sulfur. Soluble sulfides can be titrated with ferricyanide at pH 9.2 with ferrous dimethylgloxime complex as indicator (*42*). Sulfur is distilled as hydrogen sulfide into excess calcium oxychloride and back-titrated iodometrically (*152*). Adaptation of known methods (*2, 89, 109, 223*); precipitation of sulfate as lead sulfate and, after filtering, titration of excess lead with ammonium molybdate (*106*). Persulfate can be titrated with iodine in presence of cuprous iodide as catalyst (*162*).

Tellurium. Potentiometric titration with chromous ion (*123*).

Thallium. Thallous ion can be titrated with potassium iodide, using bromophenol blue as indicator (*132*).

Thorium. Iodate precipitation, followed by iodometric titration after filtering and dissolving, but not so accurate as gravimetric (*130, 190*); precipitation as molybdate which after filtering and dissolving is run through Jones reductor and Mo (III) titrated with cerate ion (*11*).

Tin. Reduction with antimony (*137*) or nickel in a hot solution (*185*) followed by iodometric estimation.

Titanium. Study of conditions for potentiometric titration of Ti (IV) with chromous ion, using mercury indicator electrode (*159*).

Tungsten. Investigation of variables in use of chromous solutions to reduce tungsten followed by back-titrating with dichromate (*205*). Solid barium thiosulfate monohydrate is used to precipitate tungsten in a neutral solution in ethyl alcohol, which is filtered, and thiosulfate in solution is titrated with iodine (*173*). Precipitation as 8-hydroxyquinoline followed by bromometric titration (*8*); review of existing methods (*26*).

Uranium. Uranyl ion is reduced electrolytically to U (IV) and titrated with cerate ion after oxidizing U (III) to U (IV) by air (*195*).

Vanadium. Reduction study of V (V) to V (IV) in the silver reductor (*122*); 8-hydroxyquinoline precipitation followed by bromometric titration (*8*); ferrous ion titration of Cr (VI) and V (V) followed by oxidation of V (IV) to V (V) with permanganate and subsequent titration with ferrous ion (*14, 52*); variations in known methods for specific materials, steel (*171*), cemented carbides (*202*), and mixtures (*34, 148*).

Water. Modification of Karl Fischer method in chloral (*182*), food (*177*), and lecithin (*21*); liquid sulfur dioxide (*51*); naval stores (*77*); micromodification (*114*); review of methods (*37*).

Zinc. After complexing nickel with cyanide, amyl alcohol and carbon tetrachloride are added with diphenylcarbazone as indicator and carbon tetrachloride layer is titrated with ferrocyanide (*55, 56*). Ferrocyanide modification (*172, 180*). Potentiometric titration with alkali suggested but may have difficulties in applying (*33*). Extractive titration with dithizone for small amounts (*3, 225*).

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Volumetric Analytical Methods for Organic Compounds

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THIS review concerns volumetric methods reported as useful in the analysis of organic compounds. The methods concern determinations of various elements, of certain functional groups, or of the percentage of a compound as a component of a mixture. The literature from January 1947 to September 1948 has been surveyed. A few articles in foreign journals before 1947 are included, as they have just become available.

ANALYSES FOR ELEMENTS

CHLORINE

A rapid micromethod (*57*) for the determination of chlorine in organic compounds uses a decomposition of the sample by treatment with sodium in butyl or amyl alcohol. The reaction mixture from the decomposition is diluted with water and titrated with 0.01 *N* silver nitrate solution using bromophenol blue as an adsorption indicator. The method has given satisfactory results with hexachloroethane, *p*-dichlorobenzene, benzene hexachloride, DDT, and 1,1-dichloro-1,1,2,2-tetraphenylethane, using samples containing about 2 mg. of chlorine. While the errors are as large as in other methods, this procedure offers the advantage of being very rapid; a complete analysis, including weighing of the sample, can be carried out in less than one hour.

The analysis for halogen by the sodium in liquid ammonia method (*67*) is limited to some extent by the insolubility of many compounds in liquid ammonia. The use of sodium naphthalene in an oxygenated solvent such as ethylene glycol dimethyl ether, ethylene glycol diethyl ether, dioxane, and methyl isopropyl ether offers the possibility of obtaining greater solubility of the sample in the reaction mixture, inasmuch as these solvents are relatively high boiling. In a recently described procedure (*9*) the sample is mixed in a separatory funnel with an excess of the sodium naphthalene reagent under a nitrogen atmosphere. The formation of sodium halide appears to be instantaneous. The mixture is washed with water and the combined aqueous layers are acidified with nitric acid and titrated potentiometrically with standard silver nitrate solution, using a silver-plated platinum wire and a saturated calomel electrode with an ammonium nitrate–agar gel bridge. It appears likely that the halogen titration could also be carried out by the Volhard or Mohr method. With compounds containing active hydrogen low results are obtained, probably because of the formation of an insoluble sodium salt. The nitro group also interferes. Hexabromobenzene and 2,2-difluoroheptane do not react at all.

In order to determine chlorine in a larger number of polychloro compounds, Gregg and Mayo (*20*) used a modified combustion method.

The compound was burned with oxygen in a Vycor tube containing platinum foil in the hottest part (800° C.) and platinum disks and crushed Vycor glass in the remainder. The chlorine was absorbed in hydrogen peroxide–sodium acetate solution using a six-bulb Will-Varrentrapp absorber. The chloride ion was then titrated with standard silver nitrate in 50% acetone solution using dichlorofluorescein as the indicator according to the procedure of Bullock and Kirk (*14*). Pure known chloro compounds gave analyses checking within 2 parts in 1000.

FLUORINE

Fluorocarbons may be analyzed for fluorine (*41*) by carrying out the sodium–liquid ammonia method of Vaughn and Nieuwland (*67*) in a sealed tube at room temperature. This permits complete decomposition of polyhalogen compounds. Halide ions other than fluoride can then be determined by modification of the Volhard method. Nitrobenzene is used to coagulate, coat, and remove the silver halide from the reaction medium rather than filtration. Fluoride is determined by precipitation as lead chlorofluoride under carefully controlled conditions. This precipitate is dissolved in dilute nitric acid and the chloride is titrated by the Volhard method.

The classical Stepanow method has been used for determining fluorine in benzyl fluorides (*11*).

The sample is treated with sodium and absolute alcohol, refluxed for 48 hours, diluted with water, and steam-distilled. The fluoride in the aqueous solution is determined by titration with cerous nitrate as described by Nichols and Olsen (*43*). If the fluorine is also present in the nucleus, as fluorobenzyl fluorides, it is necessary to carry out a sodium peroxide decomposition in order to obtain total fluorine.

HYDROGEN

In a method (*40*) for determining hydrogen in fluorine containing hydrocarbons having at least one halogen atom per atom of hydrogen, the sample is pyrolyzed at 1300° in an atmosphere of nitrogen in a platinum tube. The hydrogen halide formed, usually hydrogen fluoride, is absorbed in water and determined by titration with standard sodium hydroxide. If chlorine is present, it is determined in one aliquot portion, while in another aliquot the chlorine is converted to hydrogen chloride by hydrogen peroxide and total acidity is determined. The acidity in the original sample due to hydrogen can be found by difference. This method has been applied only to compounds containing less than 2% hydrogen, but apparently should be applicable to other compounds.

NITROGEN

A few changes have been made in the Kjeldahl method for determining nitrogen. Improvements by Sobel, Hirschman, and Besman (*58*) on the aeration tubes previously used (*59, 60*) make it possible to use the Kjeldahl method to determine ammonia in the range of 10 to 200 micrograms or 1 to 10 micrograms, depending on the exact way in which the procedure is modified.

In connection with a study of the nitrogen metabolism of amphibian embryos, another useful modification of the Kjeldahl method was used (*6*). The ammonia was distilled into a standard solution of potassium biiodate, potassium iodide was added, and the solution was titrated with standard thiosulfate. A sharp end point was obtained with the starch indicator.

OXYGEN

A titrimetric determination of oxygen (*3*) in organic compounds is made possible by the following procedure:

The sample is thermally decomposed over carbon at 1120° C. in a quartz reaction tube and the resultant carbon monoxide is oxidized to carbon dioxide by iodine pentoxide. The iodine liberated from the pentoxide is oxidized to iodate, potassium iodide is added, and the iodine is determined by titration with standard sodium thiosulfate solution. This procedure and the apparatus for it are essentially those of Unterzaucher (*66*) and require less elaborate apparatus than either the complete combustion method or the catalytic hydrogenation method. Special carbon must be used to avoid excessively large blanks, and a high temperature furnace, capable of continued operation above 1000° C., is necessary. The presence of elements other than carbon, hydrogen, and oxygen does not affect the applicability of the method.

SILICON

Indicating some of the current fields of interest in organic chemistry is the analysis of silicon in organosilicon compounds. McHard, Servais, and Clark (*37*) recommend the Parr bomb–oxine procedure for carrying out analyses on a small number of widely varying samples of organosilicon compounds with a minimum outlay of equipment.

The sample is decomposed in the Parr bomb and converted to a solution from which aliquots are taken for analysis. Ammonium molybdate is added to an acidic solution of the sodium silicate to give a soluble yellow complex of silicomolybdic acid. A known excess of standard oxine (8-hydroxyquinoline) solution is added to this complex. The yellow precipitate is removed by filtration and the excess oxine in the filtrate is determined by titration with a standard bromate-bromide solution. It is advisable to determine an empirical factor for each analyst or laboratory, since the theoretical factor calculated from the formula and equations gives slightly low results.

SULFUR

A semimicromethod for the determination of sulfur in organic compounds (*72*) uses the Parr oxygen bomb for decomposition of the sample. The resulting sulfuric acid is precipitated as benzidine sulfate, which is removed by filtration and titrated with standard alkali. The method has been worked out so that an accuracy of 99.4 to 100.2% can be obtained with samples containing from 5 to 15 mg. of sulfur.

In a proposed micromethod for sulfur (*23*) the sample is decomposed by heating with concentrated nitric and hydrochloric acids in a sealed quartz tube. The resulting solution is evaporated to dryness in a quartz-beaker and heated on an electrically heated block at 105° to 110° C. until all volatile acids are removed. The residual sulfuric acid is simply diluted and titrated with standard alkali to a bromocresol end point. The method is rapid and gives good results with samples weighing 2.5 to 8 mg.

When the usual Pregl method of combustion of organic sulfur compounds is used, it has been found desirable to evaporate the absorption solution to dryness to remove halogen acids. The solution is made alkaline and a sulfate titration with barium chloride, using dipotassium rhodizonate as the indicator, is carried out. Sharp end points reproducible to within 0.05 ml. have been obtained by this method and no blank correction is necessary (*1*).

A micromethod for the determination of sulfur in sulfanilamide (*61*) consists of decomposing the sample by the Carius method and then titrating with barium chloride using a tretahydroxyquinone indicator and special illumination of the solution during titration as described by Ogg, Willits, and Cooper (*45*).

FUNCTIONAL GROUPS

ACTIVE HYDROGEN

An ether solution of lithium aluminum hydride has been proposed as a reagent for estimating the number of reactive hydrogen atoms in organic compounds (*29*). The moles of hydrogen liberated by the reaction

$$4ROH + LiAlH_4 \longrightarrow 4H_2 + LiOR + Al(OR)_3$$

may be estimated by use of a simple apparatus arranged to permit measurement of the increase in pressure on a manometer. It is recommended that the reaction be carried out at 0° C. The data reported on a number of different types of compounds show that alcohols, phenols, acids, and mercaptans (thiols) give excellent results and that the number of active hydrogens corresponds to that determined by use of the Grignard reagent. The new reagent has the advantage, however, of very rapid reaction, about 5 to 10 minutes being required for equilibrium with the above classes of compounds.

Amines and amides showed the expected number of active hydrogens but amines required prolonged reaction times ranging from 50 minutes for aniline to 6 hours for di-*n*-amylamine. Aromatic nitro compounds liberated hydrogen corresponding to two active hydrogens, owing evidently to a complex series of reduction products. The Grignard method also gives erratic results on aromatic nitro compounds: 1.0 to 1.9 active hydrogens. Nitromethane with lithium aluminum hydride gave 2.4 to 2.75 active hydrogens.

The new reagent must be used with caution if employed for structural determination of new compounds. Enolizable ketones give values of active hydrogen which do not check those obtained by the Grignard machine or by the Meyer bromine titration. Malonic ester shows 0.56 active hydrogen, monoalkyl malonic esters about 0.2, and ketones 0.05 to 0.08. Further data on the behavior of compounds containing activated hydrogens will be awaited with interest.

ACETYL

The method of Kunz and Hudson (*30*) for determining *o*-acetyl groups in the presence of *N*-acetyl groups has been successfully carried out on a micro scale (*2*). Certain compounds, such as D-*N*-methyl-L-glucosamine pentaacetate appear to give high results.

AMINES

Blumrich and Bandel (*12*) determined the amount of triethylamine present in admixture with diethylamine by acetylating the latter with acetic anhydride and then titrating potentiometrically the tertiary amine with a solution of perchloric acid in acetic acid. This method has been evaluated for a number of mixtures of amines (*68*). With simple *n*-alkyl amines the procedure gives good analyses for the tertiary amine present in mixtures containing primary and sceondary amines and ammonia. Small amounts of water do not interfere. For amines in which the nitrogen is attached to secondary carbon atoms, it is necessary to reflux the mixture for an hour with acetic anhydride and acetic acid. The mixture is then cooled, diluted with acetic acid, and titrated potentiometrically with a standard solution of perchloric acid in acetic acid.

The amounts of secondary plus tertiary amine in a mixture containing the primary amine may be determined by adding salicylaldehyde to a methanol solution of the sample (*69*). The primary amine reacts with the aldehyde to form an azomethine (Schiff base) with reduced basicity. Hence the unchanged secondary plus tertiary amine may be titrated potentiometrically with a standard solution of hydrochloric acid in isopropyl alcohol. The method was tested on a number of amine mixtures and found to give results averaging ±0.7% of the amount of secondary and/or tertiary amine. A modification is suggested, so that the analysis may be run on mixtures also containing ammonia.

ARSONOUS ACIDS AND ARSENOSO GROUP

Banks and Sultzaberger (*7*) studied the titration of aromatic arsonous acids and arsenoso compounds with a standard solution of iodine and found the reaction to be stoichiometric between pH values of 2 to 6.8.

$$ArAs(OH)_2 + I_2 + H_2O \longrightarrow ArAsO_3H_2 + 2HI$$

Arsonic acids did not interfere and the titration was not appreciably affected by the presence of less than 8% of arsenic trioxide at a pH of 2 to 3. The method is therefore of great value in determining the purity of arsenicals containing the arsenoso group and arsonous acid grouping.

CARBOXYLIC ACID SALTS

The determination of carboxylic acid salts by ignition to the carbonate followed by titration of the carbonate has been successfully applied to a wide variety of sodium, potassium, calcium, and barium salts (*56*).

It has been found best to dissolve the ignited sample in a known excess of standard acid, boil to remove carbon dioxide, and then titrate the excess acid with standard alkali. With sodium and potassium salts, sulfuric acid is suitable and phenolphthalein is used as the indicator. Because of the insolubility of calcium and barium sulfates it is preferable to use hydrochloric acid instead of sulfuric and replace the phenolphthalein with methyl red. Of all the salts analyzed, only potassium acetate gave difficulty. It is so deliquescent that accurate weighings cannot be made.

The work of Hurka (*24*) is also of interest in connection with the determination of carboxyl groups. In comparing titrations of acetic acid with alkali, with ethanolamine, and by iodometric and potentiometric methods it was found that the iodometric method gave the best results.

CHLOROHYDRINS

Sodium carbonate will hydrolyze certain chlorohydrins to the corresponding glycols without hydrolyzing aliphatic chlorides, while sodium hydroxide will hydrolyze both aliphatic chlorides and chlorohydrins. This difference in reactivity is the basis of a method (*65*) for determining mixtures of inorganic chloride, chlorohydrin chloride, and aliphatic chloride. In the method three aliquots of a sample are titrated, the first without further treatment, the second after sodium carbonate hydrolysis, and the third after sodium hydroxide hydrolysis. The chloride in each aliquot is determined by the Mohr method and the compound or mixture must be in a water-soluble solvent for determination. Compounds which have been determined by this method include ethylene chlorohydrin, propylene chlorohydrin, dichloroethyl ether, dichloroisopropyl ether, ethylene dichloride, and propylene dichloride. No mention is made of the reactivity of aromatic chlorides or of allyl or vinyl chlorides under the conditions of the procedure.

DIAZO GROUPS

Various analytical procedures have been combined by Shaeffer and Becker (*53*) to obtain analyses of diazo compounds such as diazodinitrophenol (4,6-dinitrobenzene-2-diazo-1-oxide). By treating the sample with an excess of titanous chloride the diazo nitrogen is quantitatively eliminated and can be measured in a gas buret. A modified Kjehldahl method is used to determine the combined nitro and amino nitrogen. The titanous chloride volumetric method of Becker (*8*) is used with only slight modification to determine nitro nitrogen in products whose content of diazo nitrogen is known.

HYDROXYL

Hydroxyl determinations in alcohols, glycols, oils, and fats (*25*) have been carried out using a standard solution of acetyl chloride in toluene as the reagent. A special apparatus is described which excludes moisture and has a trap containing a measured amount of standard sodium hydroxide solution in order to prevent the loss of volatile hydrogen chloride or acetic acid. The mixture is refluxed for 2 hours, cooled, and titrated with standard alkali.

Another method (*15*) for estimating alcoholic hydroxyl groups consists in heating the sample with phthalic anhydride and pyridine at 100° C. Most alcohols react quantitatively within 1 hour. The titration of the reaction mixture with alkali compared with that of a blank is a measure of the hydroxyl groups present. It is necessary to heat glycerol for 2 hours to get good results. Phenolic hydroxyl groups do not react. Certain diols which dehydrate readily in the presence of an acid catalyst give poor results. Secondary amines can be determined satisfactorily by this method, but primary amines give high results, due, probably, to phthalimide formation. The method is useful in that it gives good results with fairly dilute aqueous solutions of alcohols.

OXIRANE GROUP

The method of Nicolet and Poulter (*44*) for the determination of oxirane compounds has been extended to a variety of such compounds (*62*). The method involves the reaction of the oxirane compound to be analyzed with a standard solution of hydrogen chloride in dry ether to give the corresponding chlorohydrin. The excess hydrogen chloride is then determined by titration with alkali. If the compound to be analyzed contains any acidic groups, a correction must be made for the alkali consumed by them in the titration of the excess hydrogen chloride. The method is applicable to mixtures encountered in air oxidation reactions. No difficulty was encountered in handling and storing the 0.2 *N* hydrogen chloride–ether solution used.

PEROXIDES

In studies (*71*) on the determination of organic peroxides it has been found that the method based on the reduction of peroxides with ferrous thiocyanate, followed by titration of the resulting ferric thiocyanate with a standard titanous solution, gives low results. On the other hand the iodometric determination of organic peroxides has been improved by using sodium iodide in isopropyl alcohol (*70*). This modification gives the method a more general applicability and comparative freedom from interference by atmospheric oxygen. Under these conditions iodine does not add to mono-olefins and in the absence of peroxides does not add to diolefins.

UNSATURATION

Such standard methods as bromine addition and iodine addition for the determination of unsaturation have been modified. A method which gives satisfactory results for the olefins present in gasoline, kerosene, and gas oil uses acetic acid as a solvent and a slight excess of bromide-bromate solution (*26*). The excess free bromine is determined by adding potassium iodide, and the iodine liberated is then titrated with thiosulfate. The method is not intended for cracked products which may contain branched olefins. The slow addition of bromine to stilbene and related compounds does not affect the application of the method to petroleum products, as stilbene-type compounds are not present.

In using the modified Wijs method for iodine numbers, the volume of Wijs solution required becomes of considerable importance when hundreds of determinations have to be made. This difficulty has been avoided by reducing the volume of Wijs solution used and using unstoppered flasks (*22*). The results obtained in this way do not differ significantly from those obtained using the A.O.A.C. method, and the saving on solution is fairly great. Thus, with a 0.1-gram sample of a nonconjugated fat or oil having an iodine number of less than 200, 10 ml. of Wijs solution are sufficient.

The usual Wijs procedure gave low iodine values when applied to the vinyl esters of fatty acids from caproic to stearic. However good results could be obtained by allowing the solutions to stand 24 hours or by using a 20% excess of the Wijs solution and 1-hour reaction time (*63*). Good values on methallyl, allyl, 3-buten-2-yl, and crotyl esters of fatty acids were obtained.

In addition to the determination of simple olefins, the determination of unsaturation in synthetic and natural rubber has received the attention of several investigators. A rather elaborate procedure (*33*) has been worked out using iodine monochloride as the agent adding to the unsaturation. When an excess of iodine monochloride is added to a sample of a polymer, besides the addition to unsaturation, two other reactions, substitution and "splitting out," take place, giving rise to the formation of acid. It has been shown that 90 to 95% of the double bonds in the polymer add iodine monochloride within several minutes at room temperature and that splitting out also takes place during the first few minutes of the reaction. Therefore the acid which forms after the first few minutes must be due to substitution. Using these principles, a method has been worked out which gives values of unsaturation that are corrected for substitution and are independent of the reaction time within wide limits. Although the procedure is fairly complex, it can be simplified when working with a particular type of polymer or copolymer, so that the more elaborate procedure need be used only in developing a routine procedure for a new type of polymer.

As a result of the importance of such vinyl monomers as ethylvinylbenzene, divinylbenzene, vinyltoluene, and methylstyrene which are obtained from the dehydrogenation of alkylbenzenes, a new method of determining unsaturation has been devised (*38*).

> This method is based upon the addition of mercuric acetate rather than halogen to the double bond and is particularly useful for compounds of the type mentioned because they undergo halogen substitution easily. The compound to be analyzed is treated with an excess of mercuric acetate dissolved in 40% aqueous dioxane to increase the solubility of the addition compound. The excess mercuric acetate is converted to mercuric oxide with sodium hydroxide solution and then to free mercury with 30% hydrogen peroxide. The excess mercury is thus removed from the system. The addition compound is decomposed by treatment with acid and the mercuric ions liberated are titrated with standard ammonium thiocyanate using ferric alum indicator. All reagents must be halide-free.

Nitrogen tetroxide has found use in the analysis of mixtures of olefins with saturated hydrocarbons (*51*). Two methods have been proposed. In one, nitrogen tetroxide is passed into the chilled sample and, after decomposition of the excess reagent with urea, the unreacted hydrocarbons (saturated) are steam-distilled and the volume of the hydrocarbon layer is measured. In a second method, the nitrosates formed by treatment of the sample with nitrogen tetroxide are allowed to react with alcoholic potassium hydrogen sulfide solution and the unreacted hydrocarbons are measured directly in the modified Babcock bottle in which the reaction is carried out. Both methods appear to give good results. The second method is preferred when only the volume per cent olefins is desired, because of its speed and simplicity.

In polymers prepared from 1,3-dienes there may be two types of double bonds. Internal double bonds result from 1,4- addition, while 1,2- addition gives rise to terminal or vinyl double bonds. The relative amounts of internal and terminal double bonds in a polymer have considerable bearing on the nature of the polymer. Methods for determining internal and terminal unsaturation have been based on the difference in the rate of reaction of benzoyl peroxide with the two types of bonds. The method offers a satisfactory alternative to the use of ozonolysis or infrared spectra for the same purpose. Analytical applications have been worked out by Kolthoff and Lee (*28*) and by Saffer and Johnson (*50*). One of the principal difficulties is the necessity of separating the contributions of the internal and terminal double bonds to the addition reaction, for there will be some reaction with terminal double bonds, even though it is a slower reaction. Saffer and Johnson (*50*) have proposed a unique solution to this problem.

The sample is treated with a chloroform solution of perbenzoic acid and the excess is determined iodometrically. The apparent per cent of double bonds reacted is plotted against time. The rate curve for a polymer containing both internal and terminal double bonds will be made up of the two curves for the simultaneous second-order reactions—i.e., the reactions of perbenzoic acid with internal bonds and with terminal bonds. The rate constants are different and the rapid reaction with internal double bonds will be complete when only a small part of the terminal double bonds have reacted. After all the internal double bonds have reacted, the rate curve will be that for terminal double bonds only. If the concentration of terminal double bonds is low and their reaction slow, the rate curve will be approximately linear in its later phases. Extrapolation of the portion of the curve to zero time subtracts the contribution of the terminal double bonds present.

This method was found to give good results as long as the sample to be analyzed contained 70% or more internal double bonds. The procedure is convenient and suitable for routine analysis, because a reaction can be started at the close of one day and by the next day the samples removed for analysis will give results on the linear portion of the rate curve.

The procedure of Kolthoff and Lee (*28*) is based upon the fact that the total amount of double bonds reacting in a given time will be dependent on the relative amounts of external and internal double bonds present.

It is first necessary to determine the amount of total unsaturation in the sample, so that a solution of 0.02 *M* in double bonds can be made up for the analysis. This solution is then allowed to react with standard perbenzoic acid solution for a given length of time (7 hours for butadiene polymers). The perbenzoic acid consumed is determined iodometrically and the percentage of double bond reacted is calculated. The amount of external double bonds is then read from a calibration curve. The method has been applied to butadiene and isoprene polymers and to butadiene-styrene copolymers.

MISCELLANEOUS METHODS

A method for the determination of high molecular weight quaternary ammonium compounds is based upon the formation of triiodides (*21*). A solution of the triiodide may be determined colorimetrically, or acidified and titrated with sodium thiosulfate. In the latter case only two of the three iodine atoms are available for oxidation of the thiosulfate.

One of the two double bonds of dicyclopentadiene adds various reagents fairly readily. The reaction with formic acid has been employed in the determination of dicyclopentadiene (*10*). The product, dicyclopentenylformate, is determined by its saponification equivalent, and from that value the percentage of dicyclopentadiene can be calculated. The method is reliable to about 0.5% and impurities present in technical dicyclopentadiene do not interfere. Higher polymers of dicyclopentadiene react with formic acid, however, so that mixtures containing higher polymers must first be separated by fractional distillation.

Hydrocarbon gases in the four-carbon range have been analyzed for ethylacetylene and vinylacetylene (*64*) by the following scheme.

Total acetylenes are determined from the acidity produced when a sample is treated with 2.5% silver nitrate solution. Catalytic hydrogenation is used to differentiate between ethylacetylene and vinylacetylene after corrections have been made for the hydrogen consumed by the olefins and 1,3-butadiene. Olefins plus 1,3-butadiene are determined by bromine addition and 1,3-butadiene by the use of maleic anhydride. Ethylacetylene and vinylacetylene are determined with an average deviation of 0.8% on the basis of the total sample over a concentration range of 1 to 100%. Methylamine and methanethiol interfere and, if present, must be removed before the determination is made. 1,2-Butadiene also interferes, but no chemical method is available for its determination. The apparent percentage of vinylacetylene will be increased and consequently the ethylacetylene will be decreased by the amount of 1,2-butadiene that is present.

Periodic acid, a valuable tool for structural determinations in organic chemistry, has been applied to the quantitative determination of glycerol in fermentation residues (*16*). The formaldehyde formed by the periodic acid oxidation of the glycerol is determined by the sulfite method of the A.O.A.C. (*5*) or it may be determined polarographically. This method is somewhat similar to that of the A.O.A.C. for glycerol in wine and the simpler method of Amerine and Dietrich (*4*), but these methods cannot be applied successfully to fermentation residues. Presumably this method could be modified to fit the analysis of other glycols.

A method for determining β-dicarbonyl compounds (*52*) has been worked out using acetylacetone, ethyl acetylpyruvate, and sodium ethyl acetylpyruvate, and it appears likely that the method can be applied with only slight modification to other β-dicarbonyl compounds. The β-dicarbonyl compound is mixed with a standard cupric acetate solution and the copper derivative which precipitates is removed by filtration. Since precipitation of the complex is not complete, the copper complex remaining in the filtrate is removed by extraction with chloroform. The excess cupric acetate in the filtrate is determined iodometrically and the amount of carbonyl can be calculated from the amount of copper consumed. By careful control of the pH, acetylacetone containing acetoacetic ester can be determined without interference from the acetoacetic ester.

In order to avoid using Zeisel determinations or saponification equivalents to determine the degree of reaction or degree of substitution in polyallyl ethers and polyallyl esters, the following methods for determining unsaturation have been tried (*13*): rapid Wijs, 1-hour Wijs, Kaufmann (*27*), Rosenmund and Kuhnhenn (*49*), and direct bromine titration. From experiments run on allyl phthalate, allyl acetate, triallyl glycerol, allyl starch, and allyl sucrose it is concluded that numerous methods can be used to determine the number of allyl groups in a polyallyl ether or ester. The simplest and most rapid method is the rapid Wijs (only 4 minutes), which in all cases gave values less than 1% lower than theoretical.

The method of Widmaier (*73*) has been applied to the determination of tetraethyllead in aviation gasoline (*42*). The method is based upon the following reaction of tetraethyllead with iodine:

$$Pb(C_2H_5)_4 + I_2 \longrightarrow Pb(C_2H_5)_3I + C_2H_5I$$

A known excess of iodine in potassium iodide is added to the sample. The excess iodine is then determined by titration with sodium thiosulfate.

The rather complicated problem of determining vinyl ethers and acetals and any alcohol, acetaldehyde, and water contained in them has been worked out by Siggia (*54*). The analyses are obtained by a combination of hydrolysis, hydrogenation, the acetic anhydride method for hydroxyl, the Karl Fischer reagent, and the sodium sulfite–sulfuric acid method for aldehydes.

Vinyl alkyl ethers may also be determined by an iodometric method (*55*). Iodine and methanol are added to the vinyl alkyl ether to be determined to give methyl alkyl acetals of iodoacetaldehyde. The excess iodine is determined by titration with standard thiosulfate solution. This method is of particular value for samples containing acetaldehyde or acetals, since all previous methods depended on hydrolysis of the ether to acetaldehyde and its subsequent determination. The reaction time for the analysis is only 10 minutes and the average deviation is 0.2%. Lauryl vinyl and octadecyl vinyl ethers could not be determined because of their insolubility in the reagents used.

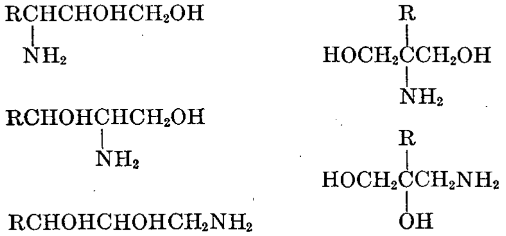
The use of cinnamoyl chloride for the determination of water has been studied (*35*). The hydrochloric acid liberated by the reaction between cinnamoyl chloride and water can be titrated with standard alkali. High blanks are required because of the high moisture content of the acid chloride. In some cases (*36*) the cinnamic acid formed reacts with the cinnamoyl chloride to form the anhydride and liberate hydrochloric acid. It appears that naphthoxychlorophosphine is superior to cinnamoyl chloride for the determination of water (*34*). As much as 25 to 30 mg. of water can be determined with 1 gram of this reagent.

Continued interest is shown in the analysis of insecticides. A simple method (*18*) for determining 666 (hexachlorocyclohexane) in cloth consists of extracting the 666 from the cloth with acetone in a Soxhlet extractor, dehydrochlorinating the extract with 0.3 *N* sodium hydroxide, and then determining the liberated chloride by the Volhard method. If chlorinated paraffins are used as a binder in the cloth, they will interfere. This can be corrected for by running a blank on cloth containing the binder but not the 666. Recoveries of 97 to 98% are obtained with the best procedures. The incomplete recovery may be due to the presence of the β- isomer which is dehydrochlorinated with difficulty.

The difference in the rate of dehydrochlorination of isomers of hexachlorocyclohexane in ethanolic potassium hydroxide is such that the α- and δ- isomers can be almost completely dehydrochlorinated before the γ- isomer loses any chlorine. This difference in behavior is the basis for the determination of the γ- isomer (*31*). Dehydrochlorination for a long period of time removes the halogen from the α-, δ-, and γ- isomers. As the β- isomer is inert under these conditions, the difference in chloride produced in a definite short period (15 minutes) and a definite long period (50 minutes) is a function of the amount of γ- isomer present. The chloride removed in the dehydrochlorination reaction is determined by the Volhard method. This method is not applicable to mixtures containing DDT, DDD, chlorinated camphene, chlordan, or other insecticides containing labile chlorine.

The determination of 2,4-dichlorophenoxyacetic acid (2,4-D) in commercial herbicides is accomplished simply by titration of the acid (*48*). If the acid is in the form of an ester, amide, or salt, these are first hydrolyzed to the acid and then titrated with alkali. If results are high because of the presence of other acidic groups in the commercial preparation, a check can be made by analyzing for total chlorine providing that there are no other chlorine compounds present.

The following five different types of dihydroxyaminoalkanes



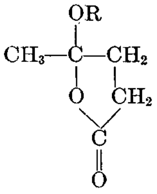
$\mathrm{R\underset{NH_2}{\underset{|}{C}}HCHOHCH_2OH}$ $\mathrm{HOCH_2\overset{R}{\overset{|}{\underset{NH_2}{\underset{|}{C}}}}CH_2OH}$

$\mathrm{RCHOH\underset{NH_2}{\underset{|}{C}}HCH_2OH}$ $\mathrm{HOCH_2\overset{R}{\overset{|}{\underset{OH}{\underset{|}{C}}}}CH_2NH_2}$

$\mathrm{RCHOHCHOHCH_2NH_2}$

may be qualitatively and quantitatively determined by oxidation with periodate (*39*). An aqueous solution of the aminoglycol is treated with an excess of a solution of potassium metaperiodate. After 20 minutes a borax–boric acid buffer solution and potassium iodide are added and the liberated iodine is titrated with standard sodium arsenite. In order to distinguish different types of aminoglycols, formaldehyde, and/or acid and ammonia must also be determined.

Pseudoesters (I) of levulinic acid may be distinguished from normal esters (II)



I

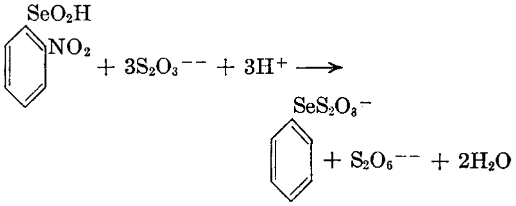
$CH_3COCH_2CH_2CO_2R$

II

by their sensitivity to hydrolysis (*32*). Advantage of this fact is taken to determine the percentage of pseudo and normal esters in a mixture. The psuedoester is stirred with water at 50° C. for a few minutes, cooled, and titrated with 0.1 *N* alkali. Total esters are determined by boiling with alkali and the difference represents normal ester.

The piperazinium salts of a large number of organic acids may be satisfactorily titrated in 50% aqueous isopropyl alcohol using 0.1 *N* sodium hydroxide solution and either thymophthalein or Orange II as the indicator (*46*). The rate of reaction of ascorbic acid or of α-hydroxytetronic acid with aqueous formaldehyde may be followed by measuring the carbon dioxide evolved (*47*).

o-Nitrobenzeneseleninic acid may be readily estimated by adding an excess of standard sodium thiosulfate solution to a slightly acid solution and then titrating the excess thiosulfate with iodine (*17*). The reaction is:



1,2,3,4-Tetrahydro-2-naphthol is extracted from cloth with ether and then determined by the acetic anhydride–pyridine method, using a mixed indicator of thymol blue and phenolphthalein (*19*).

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[End of Review Section]

Determination of Lithium in Rocks by Distillation

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A method for the quantitative extraction and recovery of lithium from rocks is based on a high temperature volatilization procedure. The sample is sintered with a calcium carbonate–calcium chloride mixture at 1200° C. for 30 minutes in a platinum ignition tube, and the volatilization product is collected in a plug of Pyrex glass wool in a connecting Pyrex tube. The distillate, which consists of the alkali chlorides with a maximum of 5 to 20 mg. of calcium oxide and traces of a few other elements, is removed from the apparatus by dissolving in dilute hydrochloric acid and subjected to standard analytical procedures. The sinter residues contained less than 0.0005% lithium oxide. Lithium oxide was recovered from synthetic samples with an average error of 1.1%.

THE accurate determination of lithium in rocks is not easy, even after the alkalies have been obtained in a comparatively pure solution. The analysis is further complicated by the laboriousness of the classical methods for isolating the alkalies, which is chiefly due to the large amounts of reagents that must be used for purposes of decomposition. Although unsatisfactory from various viewpoints, the ancient methods of Berzelius (*2*) and Smith (*8, 9*) and their recent modifications (*5, 6, 10*) are the best now available for accurate work.

The inadequacies of the well-known methods for separating the alkali chlorides before determination of lithium in rocks have been ably discussed by Kallmann (*5*), who has pointed out the losses inherent in each step of the various procedures. He has combined the best features of the Berzelius method (*2*) as modified by Koenig (*6*) and of the J. L. Smith method (*8, 9*) and has overcome most of the error by careful reworking of all residues and precipitates. Nevertheless, these methods suffer from the disadvantage of requiring separation of large amounts of impurities in the solid state from small amounts of alkalies in the filtrates.

The method described below is a radical departure from current procedures. It utilizes high-temperature volatilization for an immediate and relatively clean separation of lithium and other alkalies from the sample. It is an adaptation for analytical purposes of the Fraas-Ralston (*3*) commercial process for the production of lithium salts from spodumene. In the proposed procedure, the sample is sintered with a calcium carbonate–calcium chloride mixture at 1200° C. for 30 minutes in a platinum ignition tube through which a current of air is drawn. The volatilization product is collected in a plug of glass wool in a connecting Pyrex tube, which is then washed out with dilute hydrochloric acid. The resulting solution is subjected to standard procedures for the determination of lithium.

This paper is concerned primarily with the quantitative extraction and recovery of lithium from its various minerals, although use of the method in determining other alkalies is also proposed. Because lithium is accompanied by other ions in the volatilization step, the composition of the distillates is discussed. However, the separation of these ions and the final determination of the lithium are of secondary interest, as both may be accomplished by standard procedures.

REAGENTS AND APPARATUS

Calcium carbonate, C.P., lithium-free. Calcium chloride, C.P., anhydrous, lithium-free.

The apparatus is shown in Figures 1 and 2.

A is a platinum–10% rhodium ignition tube (0.3-mm. wall thickness) with small end tapered to fit inside *B*, a Pyrex standard-taper female interjoint 9/14, with small water condenser sealed on exit end.

C is a plug of Pyrex wool. *D* is a platinum–10% rhodium boat, 15 × 83 × 7 mm., 0.3-mm. wall thickness. *E*, crystal corundum pedestals for boat, were made from sections of a boule of synthetic corundum.

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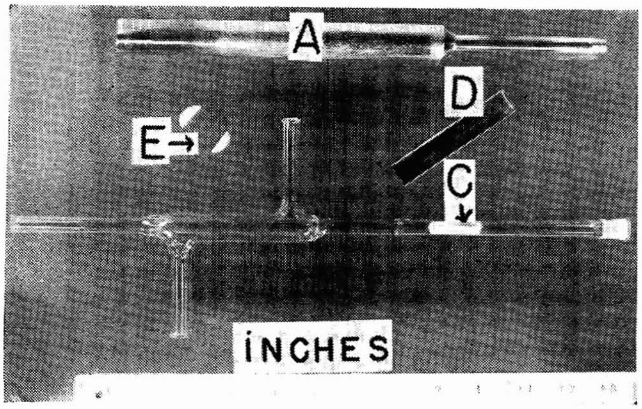

Figure 1. Unassembled Apparatus

F is a platinum-wound furnace with Variac (Type 100 Q) and ammeter. Its over-all length was 30 cm. (12 inches), and inside diameter 0.875 inch. An Alundum tube was used on which 5 inches of 20-gage platinum 10% rhodium resistance wire were wound 10 turns per inch.

The optical pyrometer is not shown in the photographs.

METHOD

Mix 2.9 grams of calcium carbonate, 1.000 gram of sample ground to −100 mesh, and 0.56 gram of calcium chloride in an agate mortar, transfer quantitatively to the platinum boat to which corundum pedestals have been affixed with an organic cement, and insert into the ignition tube. Apply full suction from a water pump to the exit end of the condenser tube and a current of cooling air to the platinum-glass joint. Start the furnace, and after a temperature of 1200° C. has been reached, maintain it for 30 minutes. Then turn off the electric current, and in about 15 minutes when the furnace has cooled to approximately 700° C. remove the boat and sinter residue. Discontinue the suction and the air current, remove the ignition tube from the furnace, and allow to cool.

Disconnect the platinum and glass parts and rinse the corundum pedestals and main portions of the assembly with dilute hydrochloric acid, to dissolve the volatilized chlorides. To do this, place the tapered end of the ignition tube in a test tube which contains a few drops of hydrochloric acid and about 25 ml. of water, police well, and rinse several times with a stream of water. The glass portion is most easily rinsed in the same test tube. Suck the dilute acid up through the glass wool plug, and then allow it to pass back down through the plug. Repeat the operation a number of times with fresh hydrochloric acid to ensure the removal of all the salts. Filter the combined solutions to separate any particles of glass wool or other extraneous matter.

Evaporate the resulting filtrate to a small volume, add 5 to 10 ml. of formic acid, and warm to reduce and precipitate platinum. Filter, evaporate the filtrate to dryness, dissolve the residue in 10 ml. of water and a few drops of hydrochloric acid, and precipitate calcium as the oxalate (*4*). Remove the ammonium salts by careful ignition, and convert the alkalies to either the chloride or the perchlorate, depending upon the choice of method for the isolation of lithium. Determine lithium in the mixed alkalies by any standard procedure. These methods have been recently reviewed by Kallmann (*5*), and the analyst may choose the one best suited to his needs.

DISCUSSION AND EXPERIMENTAL

The volatilization reaction upon which this procedure is based occurs below the boiling point of lithium chloride and depends upon the high partial vapor pressure exerted by this substance at elevated temperatures (*3*). Hence, as high a temperature as is practicable should be used. A strong current of air is necessary to remove the products from the zone of decomposition as they are formed in order to drive the reaction to completion. A platinum assembly is required, because ceramic ware is attacked by the volatilized chlorides at the working temperatures. However, because platinum sticks to platinum at these temperatures, it is necessary to employ small corundum pedestals to separate the platinum boat from the platinum tube. An Alundum boat was used to hold the platinum boat in earlier experiments, but because it absorbed about 7 mg. of lithium oxide during each run, its use was discontinued. The corundum pedestals are small and positioned well under the boat, so that the fumes apparently do not come in contact with them.

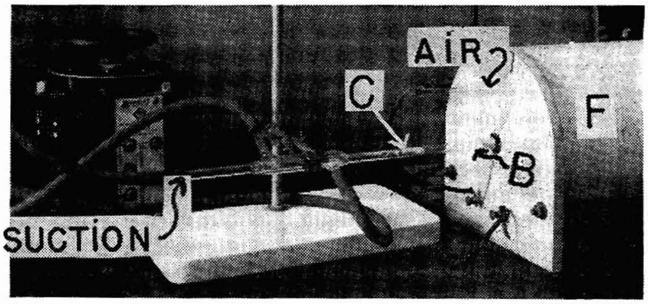

Figure 2. Assembled Apparatus

Table I. Composition of Volatilization Products from Mineral Samples

Mineral	Platinum *Mg*	CaO *Mg.*	Other Impurities, Weight Computed from Spectrographic Analysis *Mg.*
Spodumene	None	12.5	About 0.4 or less Pb, Mn, Zn, Fe combined
Lepidolite	2.4	5.9	About 0.1 Pb
Amblygonite	0.69	5.3	About 0.1 Pb, Fe combined
Petalite	0.45	13.2	About 0.4 Pb, Zn, Mn combined
Zinnwaldite	6.6	8.1	About 0.3 Zn, Mn combined
Triphylite	1.2	5.8	About 0.3 Pb, Zn combined

In assembling the apparatus, the pedestals are stuck to the platinum boat with an organic cement which is destroyed during the ignition. It is not necessary to remove the boat and pedestals as a unit, for the boat is not taken from the ignition tube until the furnace has cooled below the sticking point of platinum.

When a run is made, the sample begins to decompose between 750° and 800° C., as evidenced by the initial appearance of fumes. Although the decomposition is rapid between 850° and 950° C., it is necessary to raise the temperature to 1200° C. to remove the last traces of lithium. The temperatures listed above were measured with an optical pyrometer by sighting directly on the charge. The volatilization product collects as a white fume in the plug of glass wool, in the glass connecting tube, and in the small end of the platinum ignition tube where there is usually a small fused portion as well. The smokelike product dissolves immediately, but the fused portion requires policing to assist its solution.

The spectroscope was used to determine the completeness of the extraction of lithium from the gangue and sinter mixture, and provided a test which was simple, rapid, and a great deal more sensitive than a chemical determination. The volatilization method was tried on samples of spodumene, lepidolite, amblygonite, petalite, zinnwaldite, and triphylite and the sinter residues were examined spectroscopically for lithium; in each case the residues contained less than 0.0005% lithium oxide. The spectroscopic determinations were made on 20-mg. samples, which were completely volatilized in a carbon arc. The duration of the visibility of the 6707.9 Å. line was measured with a stop watch. Synthetic standards of approximately the same composition were used to obtain a standard curve. No claim for high accuracy is made for these determinations, and errors of 100 to 200% probably occurred; however, much larger errors than these would be necessary to invalidate the results. The residual lithium content was so small that it could not be determined chemically.

Of the samples tested, zinnwaldite fused at 1200° C., and amblygonite between 1240° and 1270° C.; but even in cases where fusion occurred, the lithium was completely removed. The volatilization product from the minerals was collected and converted to the sulfate, and subjected to spectrographic analysis to determine the impurities present (Table I). Calcium and platinum were found to be the chief contaminants and so were determined gravimetrically.

All other ions, such as aluminum, silicon, magnesium, and titanium, were found to occur in insignificant amounts. The platinum was higher in the distillates obtained from zinnwaldite and lepidolite, both of which had a relatively high potassium content. Potassium salts may be the source of the attack on the apparatus, as high platinum volatilization also resulted when a sample of Bureau of Standards potash feldspar was ignited according to the procedure.

The analyses given in Table I show lead, manganese, and zinc the chief minor impurities present in such small amounts that in most cases they can be ignored. Occasional iron would be removed with the calcium. The quantities of iron and manganese remain the same, irrespective of their original concentrations in the minerals. In the rare instances where the sample might have a high lead or zinc content, the amounts of lead and zinc found in the distillate would increase, and they would have to be removed by appropriate means, such as the ammonium sulfide method for both or the 8-hydroxyquinoline method for zinc.

Inasmuch as no direct method was available for checking the completeness of the recovery of the volatilized lithium and there were no standard samples at hand with a known lithium content, synthetic samples were prepared. To minimize errors that were not unique to the volatilization procedure itself, C.P. chemicals (Al_2O_3, 0.1885 gram; SiO_2, 0.5620 gram; and Li_2CO_3, 0.2495 gram) were used.

The purity of the lithium carbonate used was determined by analyzing six control samples for lithium by the Palkin method (*7*) as modified by Wells and Stevens (*11*). This method was also used for determining lithium in the volatilization products. The lithium carbonate was found to be 99.1% pure. Hence the amount of lithium oxide used in preparing the synthetic samples was calculated on the basis of a 99.1% pure lithium carbonate. The final lithium sulfate products obtained from the control samples were compared spectrographically with those obtained by the volatilization procedure. The products were found to be of comparable purity. The recovery of lithium oxide from the synthetic samples as determined by the volatilization procedure is reported in Table II.

The extent to which the other alkalies are volatilized has not been thoroughly tested. However, samples of Bureau of Standards analyzed soda and potash feldspars have been treated by the volatilization procedure and the residues examined with the spectrograph. Potassium could not be detected in the residues. Sodium was found to the extent of about 0.001% sodium oxide. The limit of detection of potassium is about 0.05% potassium oxide. Platinum was removed from the solutions of the volatilization products from these feldspar samples, suitable aliquots were taken, and sodium was determined by the triple acetate method (*1*). Results of determinations appear in Table III.

Table II. Recovery of Lithium Oxide from Synthetic Samples

Li_2O Present Mg.	Li_2O Found Mg.	Error, % of Li_2O Present
100.0	98.7	1.3
100.0	98.5	1.5
100.0	99.6	0.4
Mean	98.9	1.1

Table III. Recovery of Sodium from Standard Feldspars

Sample	Na_2O Present %	Na_2O Found %	Error, % of Li_2O Present
B.S. 99	10.73	10.8[a]	0.9
B.S. 70	2.38	2.30[a]	3.4

[a] Corrected for reagent blank.

If these results are typical for alkali minerals in general, the method could be extended to include analyses of all the other alkalies, for sodium chloride has the lowest partial vapor pressure of the five elements. The partial vapor pressures of rubidium and cesium chlorides are well above that of lithium chloride (*3*). In the treatment of the feldspars, fumes were first observed at 850° to 900° C. and the evolution of fumes was heavy at 1020° to 1080° C. A maximum temperature of 1300° C. was used for these volatilizations.

The total time consumed for the volatilization step in general was approximately 4 hours, about 2.5 hours of which were required to reach the decomposition temperature. All these ignitions were started with a cold furnace. The time could probably be lessened without injury to the furnace, or a furnace preheated to 500° to 600° C. could be used. If many lithium determinations were required, it would be advisable to construct a multiple-type furnace and ignite a number of samples simultaneously.

SUMMARY

A high-temperature volatilization procedure using a platinum-wound furnace has been developed for the quantitative extraction of lithium from rocks. The sample is sintered with a calcium carbonate–calcium chloride mixture at 1200° C. for 30 minutes in a platinum ignition tube through which a current of air is drawn. The volatilization product is collected in a plug of Pyrex wool in a connecting Pyrex tube and is dissolved from the apparatus with dilute hydrochloric acid. The resulting solution is then treated by standard procedures for determining lithium.

The removal of lithium from the gangue and sinter mixture is quantitative; sinter residues from spondumene, lepidolite, amblygonite, petalite, zinnwaldite, and triphylite all contained less than 0.0005% lithium oxide. Lithium was quantitatively recovered in the distillate within the range of experimental error. In a series of experiments an equivalent of 100.0 mg. of lithium oxide was added as the carbonate to synthetic samples, and 98.7, 98.5, and 99.6 mg. of lithium oxide were recovered.

ACKNOWLEDGMENTS

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Polarographic Method for Copper, Lead, and Iron

Using a Pyrophosphate Background Solution

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A linear relationship between diffusion current and concentration has been found for the reduction of copper (II), iron (III), and lead (II) in a 0.1 *M* sodium pyrophosphate solution. It is possible to utilize these complexes for analysis of several types of alloys. Because iron and lead form a single wave, one of them must be determined by another procedure if significant amounts of both are present.

COPPER (II), lead (II), and iron (III) (*10*) as well as antimony (III), uranium (VI), and other ions (*11*) appear to have analytically useful waves in a 0.1 *M* sodium pyrophosphate solution, whereas aluminum, cadmium, cobalt (II), magnesium, and nickel have waves which are not suitable for polarographic analysis either because the ion is not reduced before hydrogen is evolved or because a flat wave is formed (*10*). Although Sartori (*12*) reported that cadmium could be analyzed in a pyrophosphate background solution, his results are not clear, and the long flat wave found for cadmium by Rogers and Reynolds (*10*) would be very difficult to employ in an analytical procedure.

During the course of studies involving solutions of sodium pyrophosphate, it became desirable to establish for several ions the relationship between polarographic diffusion current and concentration. The relationships were first determined by using carefully prepared standard solutions and then checked, after devising a simple procedure, by analyzing alloys of known composition.

In a 0.1 *M* pyrophosphate solution, copper (II) is reduced in two steps having half-wave potentials of −0.40 and −1.33 volts versus the saturated calomel electrode (S.C.E.). The reductions of lead (II) to the metal and iron (III) to iron (II) have half-wave potentials of −0.69 and −0.82 volt, respectively. Therefore, in a solution of 0.1 *M* pyrophosphate containing a mixture of copper, lead, and iron, the copper waves can be distinguished easily, whereas lead and iron, which have half-wave potentials less than 0.2 volt apart, produce a single wave representing a sum of the two. Although the procedure described below does not separate lead and iron, it can nevertheless be applied to many commercially available alloys that contain a negligible quantity of either of these elements. If appreciable amounts of both lead and iron are present, another method (*5*, *6*) must be combined with the present one in order to determine the amount of each element rather than the sum.

Until 1941, polarographic procedures for alloys had not been examined extensively (*4*). More recently, a number of articles have described the application of various electrolytes, such as citrate, tartrate, or cyanide, to the analysis of aluminum- (*5*, *13*, *14*), copper- (*6*, *7*, *8*, *15*, *16*), and zinc-base (*1*, *3*, *9*, *14*) alloys. Usually the same or a slightly modified procedure can be used to analyze beryllium- and magnesium-base alloys because these elements have very negative half-wave potentials.

EXPERIMENTAL

The equipment used in this study has been described (*10*). Polarograms were recorded using a Leeds & Northrup Electrochemograph in conjunction with the calibrated dropping mercury electrode and an outside saturated calomel electrode. A thermostat maintained the temperature of the solution at 25.0° ± 0.1° C.

Standard solutions of the cations and of the sodium pyrophosphate were prepared as before (*10*). In addition, a solution of 0.1 *M* beryllium nitrate was standardized by precipitating the oxide with ammonia followed by an ignition at 1000° C. (*2*).

A solution of gum ghatti was prepared by allowing 20 grams of soluble gum ghatti from Eimer and Amend to stand in 1 liter of water for 24 hours. The resulting solution was filtered and 10 ml. of chloroform were added to prevent bacterial decomposition.

Tests of the linearity between concentration of reducible ion and diffusion current were carried out in the usual way for concentrations in the range of 10^{-2} to 10^{-5} *M* (Figure 1).

PROCEDURES

Brass Samples. A weighed sample of about 0.1 gram is dissolved in 1 ml. of concentrated nitric acid and, after the oxides of nitrogen have been expelled by boiling, the solution is made up to 250 ml. in a volumetric flask using a 0.1 *M* solution of pyrophosphate. To a 50-ml. aliquot of this solution, 1 ml. of a 2% solution of gum ghatti and 1.0 gram of solid sodium sulfite are added, following which the solution is polarographed.

Because the amount of copper in the alloy is much greater than the amount of lead, it is advantageous to use different sensitivities for determining the two elements. The amount of iron present in most commercial brasses is too small to interfere with the determination of lead. In addition, the diffusion current for iron is smaller than that of lead of the same molar concentration. As a result, the percentage of iron varied from 0.05 to about 0.2 in the five brass samples reported in Table I without interfering noticeably with the lead determination.

Table I. Analyses of Brass Samples for Copper and Lead

Sample	Weighing *Gram*	Copper, %	Lead, %
1	Stated value	75.52	6.12
	0.1103	75.5	6.2
	0.0714	75.4	6.3
	0.0482	75.4	6.3
	0.0856	75.6	6.1
2	Stated value	66.63	3.73
	0.0653	66.6	3.7
	0.1809	66.2	3.9
	0.1242	65.7	3.8
	0.1759	66.6	3.8
3	Stated value	84.17	3.76
	0.1008	84.3	3.8
	0.0642	84.4	3.6
	0.0961	84.2	3.8
	0.1162	84.1	3.7
4	Stated value	71.25	4.48
	0.1169	71.4	4.6
	0.1097	71.4	4.4
	0.0658	71.3	4.6
	0.0897	71.2	4.4
5	Stated value	70.29	0.964
	0.0782	70.4	1.0
	0.1088	70.2	1.0
	0.1656	69.2	0.9
	0.1117	69.4	1.1

Sample 5 was Bureau of Standards Brass 37; others were Thorne Smith samples.

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Aluminum- and Zinc-Base Alloys. The same general procedure was used in preparing solutions of these alloys for analysis. However, it was found best to dissolve the alloy by adding very slowly 2 ml. of 1 to 1 hydrochloric acid followed by 0.5 ml. of concentrated nitric acid. Table II gives the results of analyses on alloys from the National Bureau of Standards.

Beryllium- and Magnesium-Base Alloys. No suitable Bureau of Standard samples were on hand with which to test the method, but presumably the procedure described for an aluminum alloy could be used without modification. The absence of interferences from large amounts of magnesium and beryllium was substantiated by preparing synthetic alloys from standard solutions. A representative series of analyses of synthetic beryllium and synthetic magnesium alloys are shown in Table III.

DISCUSSION

It is very important not to add too much acid in dissolving the sample. Large amounts of acid can introduce errors by affecting the pH of the resulting solution and by causing a decrease in the amount of pyrophosphate available for complexing by converting it to phosphate. If a larger amount of acid is used to dissolve a sample, it is desirable to neutralize the excess acid by adding a solution of sodium hydroxide until a permanent precipitate is just formed. Analyses carried out using this modified procedure gave results agreeing with those listed in the tables, whereas erratic results often appeared when the bulk of the excess acid was not eliminated before adding pyrophosphate.

Every trace of oxides of nitrogen must be removed before adding the solution of pyrophosphate. In the analysis of zinc-base alloys the presence of a small amount of these oxides appeared to result in very large diffusion currents for both copper and lead. The waves had their normal half-wave potentials but the currents were sometimes 50 times higher than the expected value.

The presence of a suspension of stannic oxide did not interfere with the determination of copper and lead in brass. Furthermore, the precipitate did not appear to dissolve appreciably in pyrophosphate during the time required to make an analysis. Had it dissolved, it would not have interfered because the tin (IV) complex does not reduce before hydrogen is evolved *(10)*.

The maximum in the first wave for copper ($E_{1/2} = -0.40$ volt) spread over a wide range of potential, but it caused no difficulty in the determination of copper because the second wave ($E_{1/2} = -1.33$ volt) was usually used for this purpose. However, such an extended maximum did interfere with the determination of lead whose half-wave fell at −0.69 volt. A solution of gelatin suppressed the copper maximum but, if sufficient gelatin were added to supress the maximum completely, it also depressed the diffusion current of the lead wave to a small fraction of its true value. Gum ghatti, on the other hand, suppressed the copper maximum sufficiently well to enable a complete lead wave to be observed without at the same time noticeably affecting the diffusion current for lead.

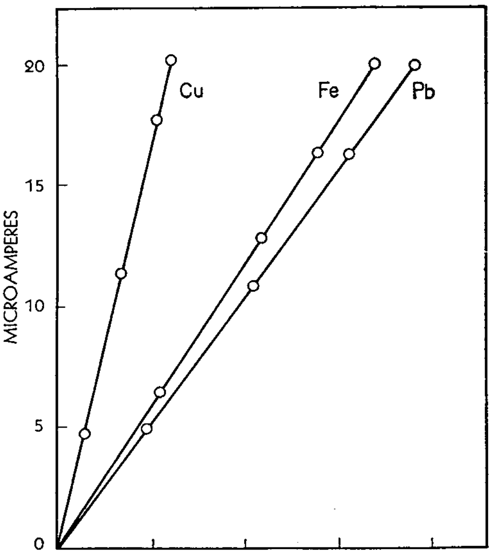

Figure 1. Linear Relation between Concentration and Diffusion Current for Copper, Iron, and Lead

Table II. Analyses of Aluminum- and Zinc-Base Alloys for Copper and Iron

Sample	Weighing *Gram*	Copper, %	Iron, %
1	Stated value	7.87	1.53
	0.0817	7.77	1.5[a]
	0.1062	7.76	1.49
	0.0432	7.9[a]	1.5[a]
	0.1172	7.88	1.56
2	Stated value	4.11	0.395
	0.1165	4.12	0.39
	0.1348	4.20	0.38
	0.1077	4.0[a]	0.40
	0.0924	4.1[a]	0.39
3	Stated value	2.82	0.048
	0.0762	2.8[a]	0.06[a]
	0.1165	2.72	0.062
	0.1342	2.76	0.050
	0.0425	2.9[a]	0.04[a]

[a] Number of significant figures in results was limited by sensitivity selected for specific polarogram.

Sample 1. Bureau of Standards aluminum-base casting alloy 86B.
Sample 2. Bureau of Standards aluminum alloy 85.
Sample 3. Bureau of Standards zinc-base die casting alloy 94.

Table III. Analyses of Synthetic Beryllium- and Magnesium-Base Alloys

Sample	Copper, %	Iron, %	
1 stated value	6.75	4.21	52.1% Be
	6.70	4.31	
	6.92	4.16	
	6.80	4.26	
	6.71	4.19	
2 stated value	3.26	1.96	87.7% Mg
	3.33	1.88	
	3.26	1.89	
	3.30	1.92	
	3.31	1.97	

The use of gum ghatti is also recommended for mixtures of copper with iron, although in this case the half-wave potential for iron (−0.82 volt) is sufficiently more negative than that for lead (−0.69 volt) to decrease automatically the interference from the maximum of the copper wave at −0.40 volt. Therefore, the amounts of gelatin required to eliminate interference from the copper maximum are too small to affect adversely the diffusion current for iron.

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Apparatus for Electrolysis at Controlled Potential

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A unitized controlled potential apparatus is described which contains a source of accurate reference potential with a range of 0 to 4.44 volts, a sensitive unbalance detector and electrode potential correcting unit, and a source of line-supplied direct current which is independent of line voltage variations. Using a mercury cathode, and with initial current as much as 100 times final current, the sensitivity to changes in electrode potential is about 1 mv. and the instantaneous deviation from the control point not more than ±10 mv.

THE apparatus described was designed to be fully automatic and as nearly foolproof as possible, for use as a routine tool in an analytical laboratory. It can be used for the preparation of samples in the systematic polarographic analysis of inorganic or organic mixtures, as well as in organic synthesis (*4*), and has been proposed as a means of direct analysis of alkali metals by separation using a rotating silver anode and mercury cathode by the method of Smith (*5*).

Earlier apparatus designed to accomplish work of this nature has been described by Hickling (*2*), Caldwell, Parker, and Diehl (*1*), and more recently by Lingane (*3*). The requirements of a routine laboratory apparatus were met by combining the best features of the above-mentioned equipment—namely, complete line operation (except for the battery in the reference potential potentiometer), wide range of voltage and current, high sensitivity, and freedom from need of operator attention and maintenance.

METHOD

A block diagram of the apparatus is shown in Figure 1. A Leeds & Northrup potentiometer, Type 7665-S with a special range of 4.44 volts, is used as a reference potential. The difference voltage between this reference voltage and that developed between the mercury or platinum cathode and a saturated calomel half-cell is detected by a Brown Electronik amplifier (Brown Instrument Company, 4482 Wayne Ave., Philadelphia 44, Pa.). The output of this amplifier controls the direction and speed, corresponding to the sign and magnitude of input unbalance, of a two-phase motor which drives a Helipot potentiometer (Helipot Corporation, 1011 Mission St., South Pasadena, Calif.). A voltage picked off the sliding arm of this potentiometer varies the grid voltage of a pair of vacuum-type rectifier tubes, the plate currents of which serve to vary the output of a saturable reactor. The reactor maintains the primary voltage of a step-down transformer supplying the low voltage rectifier at a value that provides a constant cathode potential independent of electrode current and line voltage.

APPARATUS

The entire apparatus is housed in a steel case occupying a table space 50 cm. (20 inches) long by 45 cm. (18 inches) deep. The rear 7.5 inches are occupied by the alternating current power supply and covered with a cane-pattern sheet metal cover which provides adequate ventilation as well as protection. The front section of the cabinet is made of 18-gage steel sheet and supports the Duralumin control panel on a slope of 30° running from a height of 6 inches at the front edge to 12 inches at the rear. The Brown amplifier is secured as a unit to the inside rear wall at the bottom.

As shown in Figure 2, a photograph of the complete apparatus, the Leeds & Northrup potentiometer has been removed from its case and mounted on the panel.

Mounted directly above the potentiometer are two meters with corresponding range switches used to measure electrode potential and current. The one on the left measures current on four ranges of 0.1, 0.5, 1.0, and 5.0 amperes. The one on the right (ranges changed after photographing) measures cathode-anode potential in three ranges of 3.0, 15, and 30 volts.

The upper large knob to the right of the potentiometer is the Helipot voltage control. A friction clutch between the Brown motor and Helipot shaft permits setting the electrode voltage manually when starting an electrolysis. The motor is rated at 27.5 r.p.m. and a 5 to 1 gear reduction is used to drive the potentiometer. As the Helipot has ten turns, the effective maximum speed of the slider is $\frac{27.5}{5 \times 10} = 0.55$ r.p.m.

The lower knob is the amplifier gain control, which enables the operator to adjust the amplification to the optimum value of maximum sensitivity without hunting. The potentiometer gain control mounted in the Electronik amplifier is disconnected and shielded leads are extended to the panel control.

The change in cell voltage is indicated by two pilot lamps which are mounted above the upper knob and are identified as increasing

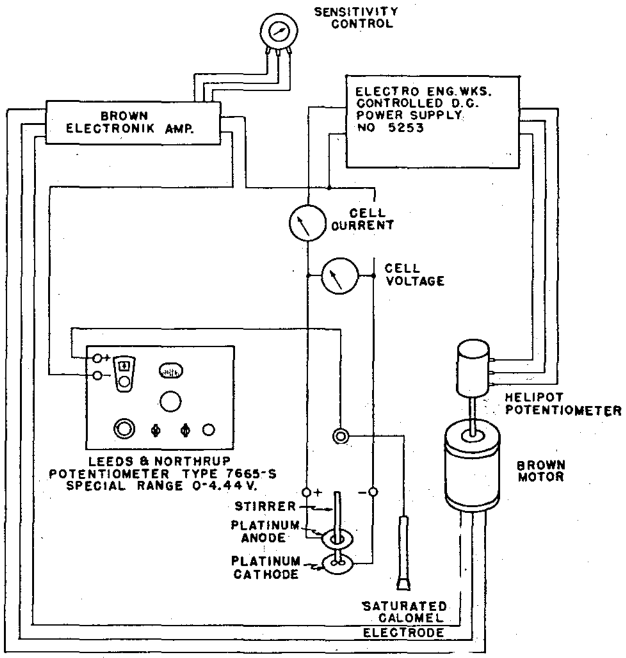

Figure 1. Block Diagram of Controlled Potential Electrolysis Unit

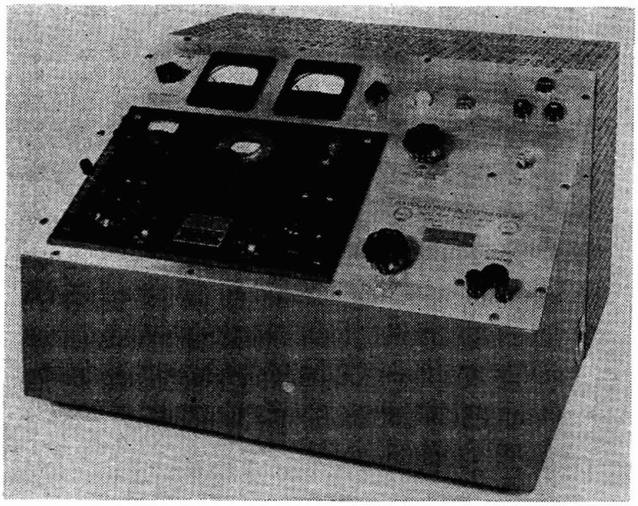

Figure 2. Controlled Potential Electrolysis Unit

and decreasing. They are actuated by a leaf-spring, single-pole, double-throw switch which has the tip of its center arm lightly in contact with the teeth of a small gear on the motor shaft. When the motor turns slowly, an indication of a slight unbalance between the reference and cell potentials, one or the other of the pilot lamps blinks slowly on and off. If the unbalance is greater and correction is more rapid, the frequency of flashing increases. An added operator convenience is the audible signal of corrective action furnished by the clicking of the switch blade on the gear teeth, although in this case there is no indication of direction.

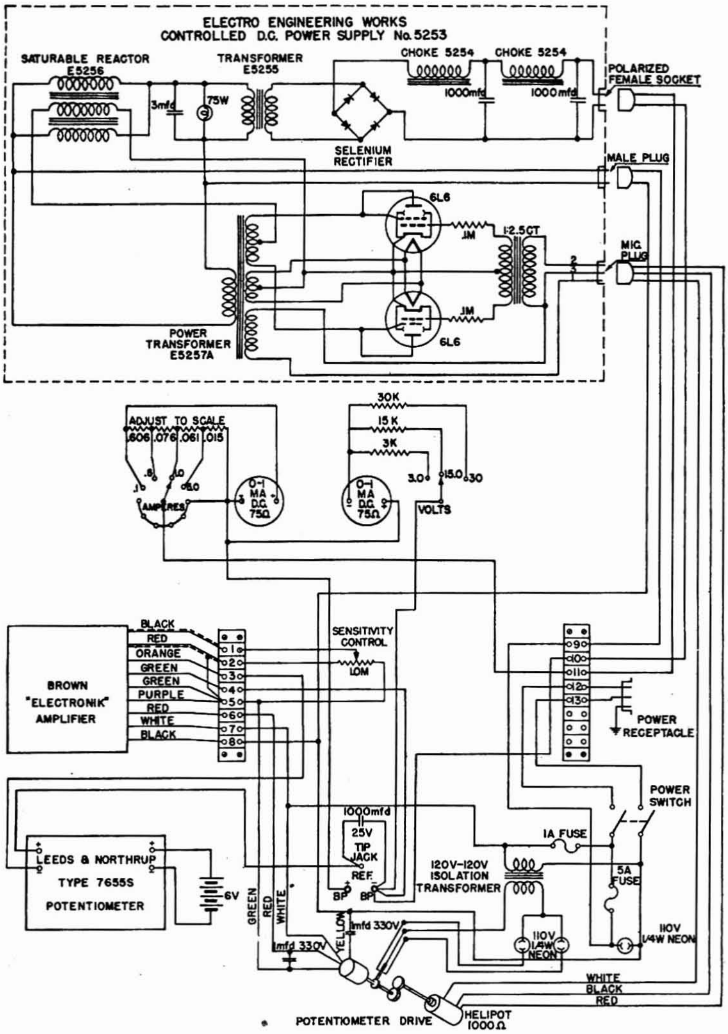

Figure 3. Wiring Diagram of Controlled Potential Electrolysis Unit

Amplifier and power supply fuses and the power switch and pilot light are located in the upper right corner of the panel.

Terminals for the electrodes, binding posts for the working electrodes, and a telephone pin jack to match a Beckman calomel electrode (National Technical Laboratories, 820 Mission St., South Pasadena, Calif.), are conveniently located in the lower right corner of the panel.

WIRING DIAGRAM

Figure 3 is a wiring diagram of the complete apparatus. The power supply can be purchased as a unit, controlled d.c. power supply, Type 5253 (Electro Engineering Works, 6021 College Ave., Oakland, Calif.). The 75-watt lamp across the primary of step-down transformer E-5255 provides an auxiliary load on the reactor, so as to retain relatively linear control when the electrode current is approaching zero. A two-section filter on the low voltage output reduces the ripple voltage to less than 0.010 volt at maximum load.

The "ring" shunt shown for the ammeter has the advantage, over individual shunts, of not including the switch contact resistance in the measuring circuit. The meter is also less susceptible to overload damage, as accidental opening of the switch contact opens the load circuit rather than the shunt circuit. Resistance values indicated are calculated and must be adjusted at assembly to the meter used.

The terminal boards shown are provided to permit individually removing the panel, amplifier, and power supply from the assembly. In addition to the seven leads of the Electronik amplifier as furnished by the manufacturer, two additional leads and shield are brought out of the case for the gain control located on the main panel.

A small transformer is necessary to isolate the voltage applied to the leaf-spring switch and neon pilot lamps from ground and the power circuit.

The 1000-mfd. condenser across the reference electrode and cathode is part of an antihunt filter. When a calomel reference electrode is used, its internal resistance makes up the resistive element. When controlling the electrode potential directly, a 1000-ohm resistor is connected between the reference electrode pin jack and the anode binding post.

OPERATION

Operation is very simple. Having once started an electrolysis, the operator may leave the apparatus unattended until the electrolysis is completed. The following steps are followed:

Insert power plug in service outlet, standardize potentiometer, connect working and reference electrodes to their respective terminals, turn on power, manually adjust electrode potential to starting value by panel knob and voltmeter, and set potentiometer to control potential and lock in galvanometer key.

The circuit will immediately start correcting, and if the sensitivity is not too high, will quickly settle down to where the lights are blinking slowly, perhaps first indicating increasing voltage and then decreasing, but finally indicating decreasing voltage only as the input potential decreases with decreasing load. If there is "hunting," the sensitivity should be decreased. Conversely, closest control is obtained at high sensitivity and the gain control should be advanced as far as possible without hunting. The galvanometer on the potentiometer should be clamped, except when standardizing, because the e.m.f. developed across its coil as it swings in the magnetic field is such as to increase the tendency to hunt.

Sensitivity may be determined by noting the number of millivolts change in potentiometer setting required to actuate the motor as indicated by the pilot lights. This can be done only when the electrolysis has proceeded to a stage where there is little change in electrode current.

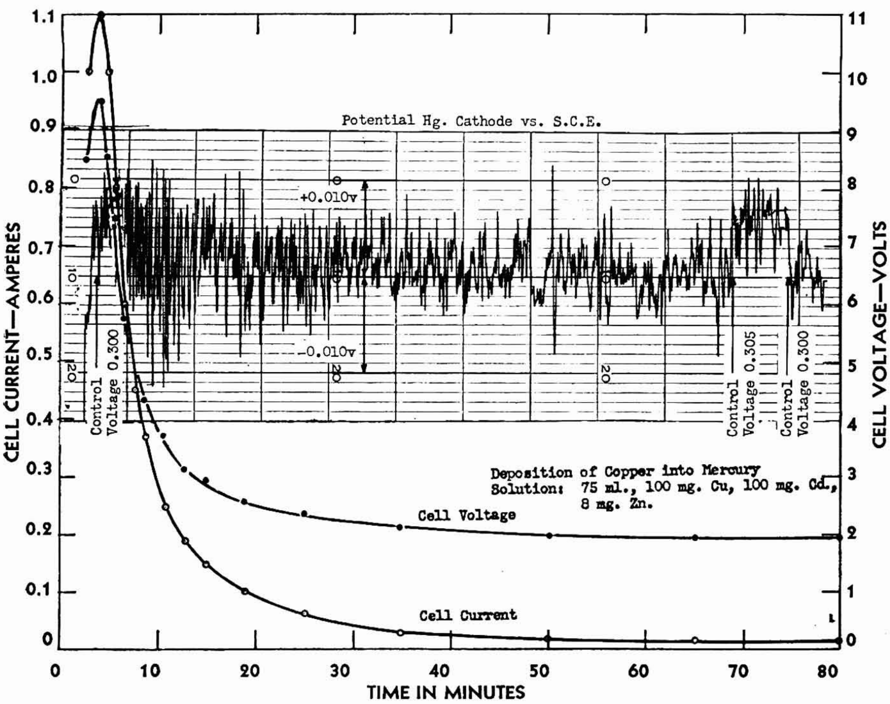

Figure 4. Control Characteristics of Controlled Potential Apparatus

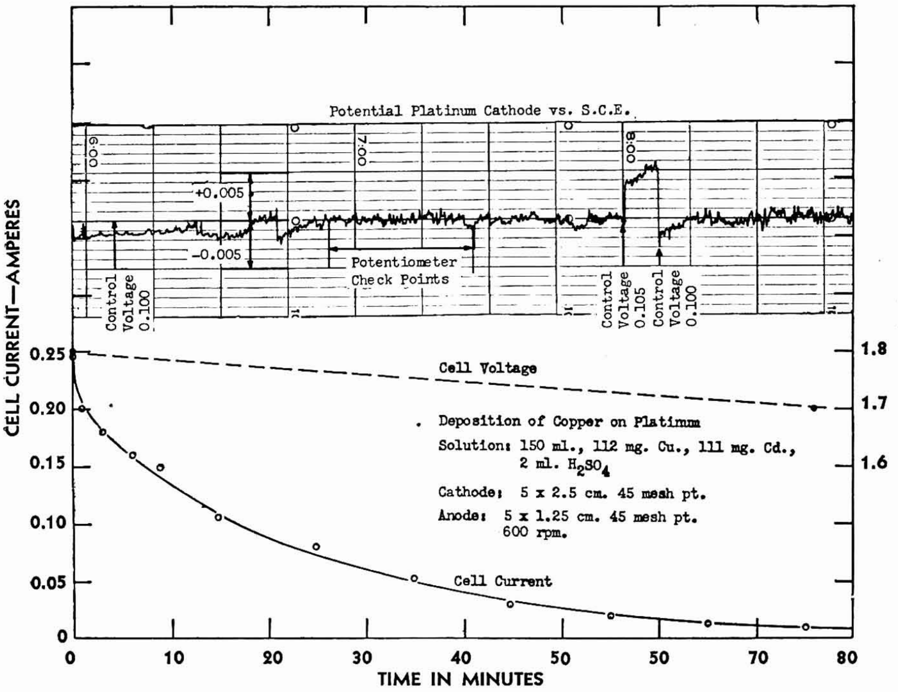

Figure 5. Control Characteristics of Controlled Potential Apparatus

EXPERIMENTAL RESULTS

Tests were made using both a mercury pool and platinum gauze as a cathode. An auxiliary potentiometer, set to the control potential, and a Leeds & Northrup Speedomax Model G recorder were connected in series across the cathode and saturated calomel half-cell so as to record the actual deviation from the control point during an electrolysis.

Figure 4 is a plot of cell voltage and current and deviation of cathode potential from the control value against time for the deposition of copper into a mercury cathode.

The electrolyte contained approximately 100 mg. each of copper and cadmium, 8.14 mg. of zinc, and less than 2 mg. of sulfuric acid in approximately 75-ml. volume. The cathode area was approximately 10 sq. cm. and the electrolyte-mercury interface was stirred by a small propeller-type glass stirrer (approximately 14 × 7 mm.) which was half in the mercury and half in the electrolyte. The stirrer revolved at approximately 1100 r.p.m. The anode consisted of four turns of No. 16 (B.&S.) platinum wire wrapped around the stirrer about 2 cm. from the surface of the mercury. The copper was first deposited at a potential of 0.300 volt *vs.* saturated calomel electrode and, although not shown on this curve, the cadmium was subsequently deposited at a potential of 0.800 volt *vs.* saturated calomel electrode.

The voltage varied from a peak of 9.5 volts 5 minutes after starting to slightly less than 2 volts in 50 minutes. In the same time the current reached a peak of 1.1 amperes and leveled off at 0.011 ampere, a ratio of 100 to 1. During this time, control was maintained within ±0.010 volt. Near the end of the runs, the control potential was shifted 5 millivolts to 0.305 volt. It can be seen from the recorder trace that a new control point was immediately established and maintained.

Deposition of copper on a platinum cathode is shown in Figure 5.

The electrolyte contained approximately 100 mg. of copper and cadmium and 2 ml. of sulfuric acid in approximately 150-ml. volume. The electrodes were 45-mesh platinum gauze; the anode dimensions were 5 × 1.3 cm. and the cathode dimensions 5 × 2.5 cm. The anode was rotated at approximately 600 r.p.m. The copper was first deposited at a potential of 0.100 volt *vs.* the saturated calomel electrode. After completion of the copper deposition, 5 grams of sodium hydroxide were added to the electrolyte and then enough acetic acid just to dissolve the precipitate. In this experiment also the cadmium was later deposited at a potential of 1.000 volt *vs.* the saturated calomel electrode. The temperature of the electrolyte during the cadmium deposition was held at 65° C.

There is markedly less fluctuation using a platinum cathode and the maximum electrode deviation from the control point is 2 mv.

ACKNOWLEDGMENT

The authors are indebted to Louis Lykken and T. D. Parks for suggesting operating requirements and to V. H. Gunther for experimental test data.

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Apparatus for Transmission Turbidimetry of Slightly Hazy Materials

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An instrument is described which measures low ranges of turbidity or haze as a ratio of the forward light scattering to the total transmission through a turbid medium. These quantities are obtained by photometering the interior of an integrating sphere by means of photocells and galvanometer when the brightness of the sphere wall is produced by the total transmitted flux, and when the brightness is reduced by permitting the unscattered fraction to escape from the sphere. Except for the possibility of Tyndall segregation, measurements are not complicated by the color of the medium. Examples of the utility of the instrument are cited, with particular reference to its application to measuring the relative specific surface of portland cement in terms of a pair of readings not involving Stokes' law.

THE measurement of turbidity of "almost clear" substances—i.e., those wherein a very small fraction of the transmitted light is scattered—may best be accomplished by an instrument in which the unscattered light may be segregated and discarded, leaving substantially all of the scattered fraction. Thus, differences in this range of turbidity which would be difficult to differentiate on the basis of total transmitted light may be significantly separated by utilizing the greater sensitivity that can be applied to the measurement of the scattered fraction only.

An apparatus fulfilling these principles was devised in these laboratories early in 1938, as a result of a need for differentiating with good precision among the clarities of "clear" nitrocellulose lacquers representing several production techniques, and in which some variation in color was also apparent. It represents a prototype from which have since been developed several different species, devised to facilitate certain particular aspects of the measurement of turbid substances.

This turbidimeter has subsequently been successfully applied to a number of additional problems where turbidity or haze was important either in itself or as a convenient index of some other property. Some of these have been: to determine the relative specific surface of powdered portland cement, to examine the resistance to air-borne abrasives of plastic lenses in gas masks, to assess the dustiness of commercial talcs, to follow the growth of bacterial cultures, and to compare the clarities of different brewings of beer. Because of the interest of a group within the A.S.T.M. of which one of the authors was a member, the possibility was examined of adopting the apparatus as part of a standard procedure for characterizing the haziness of transparent plastics. A number of similar turbidimeters have been constructed by independent laboratories, and latest data give promise that good interlaboratory concordance can be obtained.

The apparent general utility of this instrument has therefore prompted the present article.

CONSTRUCTION

The general design is such as to permit a sharply defined beam of light to pass normally through a light-scattering medium, placed against a hole centered on a horizontal axis of a hollow sphere whose interior surface is painted matte white (special sphere paint for optical integrating spheres, available from Benjamin Moore Paint Company). Upon emerging from the specimen, the unscattered light passes diametrically through the interior of the sphere to a second hole on the opposite side, through which the beam can pass, but which can also be closed to retain the light within the sphere.

Photometering the brightness of the interior surface of the sphere can be accomplished by the use of a number of well known visual and photoelectric accessories. The use of barrier layer cells and a multisensitivity galvanometer has been found convenient in this instance. Figure 1 is a photograph and Figure 2 a schematic drawing of the turbidimeter incorporating the above geometry.

The light source, 1, consists of a 50-c.p. prefocused automobile headlamp backed by a spherical mirror adjusted to superimpose on the filament its inverted image. This provides a small source of relatively uniform brightness. Two plano-convex condensing lenses, 2, focus the light to a small bright spot at a hole in the diaphragm, 3. This orifice acts as a virtual source whose image is caused to focus sharply at the exit hole of the sphere, 9, by means of the lens system, 4. All of the lenses and the lamp housing were taken from an SVE (Society for Visual Education, Chicago, Ill., Model Jr.) projector. A beam which is substantially collimated, and which also produces a circular spot of sharp definition at the exit hole, is thus provided. The use of suitable diaphragms and a coating of soot in the lens tube, 5, reduces stray light to a minimum.

The light beam emerges from the lens tube and next passes through the specimen holder, 6, and its contents, into the integrating sphere, 8, through the inlet hole, 7, which has a diameter considerably larger than the beam. The integrating sphere was formed from two chemist's sand bath hemispheres of 25-cm. (10-inch) diameter. The necessary holes were cut in these, ring flanges were welded to the peripheries, the interior was coated white, and the two halves were joined by screws through the flange, using a ring of white blotting paper as a gasket.

If the exit flap, 10, is closed, the radiation is diffusely reflected by the sphere paint on its face and is retained in the sphere. The flap consists of a metal button with a peripheral shoulder that fits closely into the exit hole. It operates within the light trap by means of a rod support upon which it is mounted, and by means of which it can be inserted or swung away from the hole by turning a knob exterior to the trap.

The brightness of the sphere wall is viewed by four barrier layer photocells, 11, connected in parallel, which are so matched to a variable sensitivity galvanometer that incident flux on the cells is proportional to the galvanometer deflection. Upon opening the exit hole, whose diameter is only slightly larger than that of the focused beam, substantially all of the unscattered light passes into the light trap, 12, and is absorbed, while any scattered fraction is retained within the sphere and measured by means of the photocells.

The photocells used (G.E. Type 88X565) are relatively too sensitive in the blue to approximate the luminosity curve for the I.C.I. Standard Observer in the event that correlation with visual experience is required (*8*). However, suitable corrective filters may be applied or cells with a more satisfactory response may be substituted. These are directly connected to a double suspension galvanometer equipped with an Ayrton shunt such that the cells are connected to a constant resistance of 300 ohms or less. Choice of inherent sensitivity of the galvanometer will depend upon the brightness produced in the sphere by the light source and the reflectivity of the interior of the sphere, coupled with the

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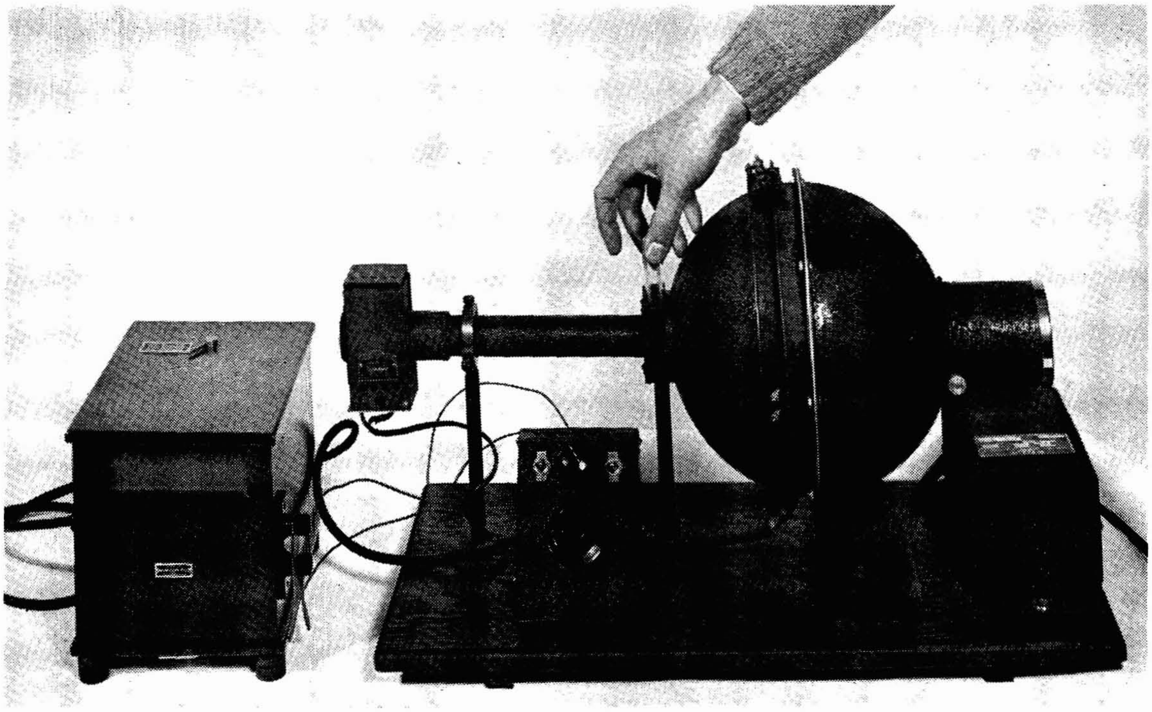

Figure 1. General View of Sphere Turbidimeter

maximum sensitivity required and the minimum sensitivity produced by the shunt. A good combination is one with a shunt reading from 100 to 1 in five steps, and a galvanometer giving slightly over a full scale reading at maximum sphere brightness and on lowest shunt sensitivity.

The light trap is a cylindrical canister containing a series of truncated cones, 13, spun from copper sheet. The end of the canister against which the light impinges carries a central cone, 14, with a surface of polished chromium plate. All of the interior except the latter cone is painted dull black; hence light is reflected specularly therefrom and is absorbed in the recesses behind the truncated cones. The reflection factor of this assembly is extremely low.

The lamp circuit is important but not complicated. Clean tight contacts, preferably soldered throughout, are necessary to eliminate fluctuation in current. In addition, a small voltage regulator is advisable to assure constancy of voltage supply. This is best followed by a small variable autotransformer, in order to obtain the minor adjustment that is helpful in setting a desirable reading on the galvanometer. The voltage supply is then stepped down to 6 to 8 volts through a transformer, thence to the lamp.

The specimen holder, which is a rectangular metal box designed to hold a specimen or cell up to 45 mm. high, 40 mm. wide, and 13 mm. thick, is attached rigidly to the sphere wall. Leaf springs maintain contact of the specimen in the proper position tangent to the sphere. The top of the holder is equipped with a lid to exclude light; a pin through the bottom aids in ejecting the specimen.

ADJUSTMENT AND OPERATION

Adjustment consists only of aligning and spacing the elements in the lens tube; first, the condensing lenses and orifice diaphragm to obtain a bright spot on the orifice, and second, the focusing lenses to produce a sharp image of the orifice at the exit hole, slightly smaller than the hole itself. These adjustments are best accomplished by setting up the lens tube assembly separately in a darkened room. For minimum stray scattering the lenses must be cleaned carefully and be without observable defects.

Upon replacing the tube, care must be taken so to align it that beam and exit hole are coaxial. This procedure is facilitated by a clamping device with adjustable thumbscrews (15, Figure 2), acting as a support of the lamp end of the lens tube. The small amount of motion of the lamp housing obtainable in this manner arises from the tolerance in the fit of the lens tube on the specimen holder. Adjustment is made for concentricity of light spot and exit hole with the holder empty and the exit flap open, turning the thumbscrews and locking them when a minimum current is obtained from the photocells. A No. 60 drill hole, placed as close to the cell holder as is convenient, has been found helpful while making this adjustment. Through this hole a clear view may be had at all times of the opposite interior wall of the sphere, including the exit hole. With the flap open, no scattering sample in place and the lens tube centered, one obtains the impression of viewing an extremely faint solar corona. The exit hole should be jet black and surrounded symmetrically by a region of faint luminescence.

In calibrating the sphere turbidimeter it is necessary to determine and minimize inherent instrument causes for galvanometer deflections and, by ascertaining the irreducible minima for any which cannot be eliminated, make certain that they are maintained as low as possible. The following procedure is recommended:

1. The galvanometer should be adjusted to read zero both at low and high sensitivity of the shunt when connected to the photocells in a darkened room. Contact potentials and dark current of the cells are thus compensated. In a lighted room a small deflection at high sensitivity will then be an indication of leakage of light into the sphere.

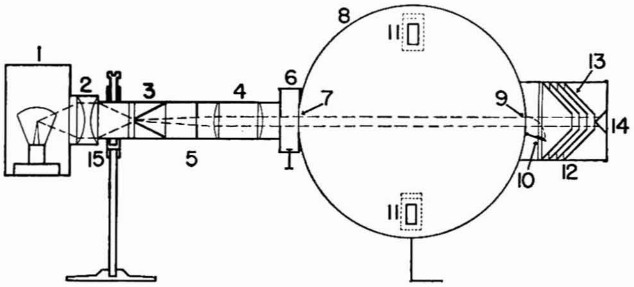

Figure 2. Diagrammatic Full Section of Sphere Turbidimeter

2. With the shunt at lowest sensitivity, the exit closed, and the lamp turned on, its current is adjusted to give approximately a full scale reading. Opening the flap and then changing the shunt to give a high galvanometer reading provides a second figure when

the latter is suitably reduced by the shunt sensitivity ratio. The second figure should be less than 3% of the first.

3. In measuring turbid liquids the scattering due to the glass cell can also be measured and taken into account. This is done by first filling the cell with a clear medium preferably similar to the suspending liquid of the turbid material. Repeating operation 2 gives a figure indicating the combined imperfections of the instrument and cell.

4. If a solid specimen should be prismatic, a correct second reading will generally not be obtained because of deviation of the unscattered beam. Simple compensation is afforded, however, by altering the position of the lens tube to give a minimum galvanometer deflection. In contrast, lens-shaped distortion of a specimen can be serious, since it is difficult to detect and can be corrected only by immersion of the specimen in a cell containing a liquid of about the same refractive index which, moreover, does not attack the substance being examined. This expedient is successful only where scattering produced in the interior of the specimen is of interest; measurement of surface imperfections, such as scratches, is defeated by their disappearance upon immersion.

DISCUSSION

Turbidimetry as a quantitative evaluating technique is over 50 years old. The earliest procedures involved making direct visual comparisons between two specimens or between a specimen and a standard material. Developments in instrumentation and elimination of systematic errors made it possible to achieve high precision for analytical chemical purposes (*13*). Limitations associated with the need for direct reading of scattering where, for physical reasons, comparison with standards was not feasible were later largely eliminated by procedures by means of which improved stability could be achieved and maintained. Human error was also greatly reduced by the adoption of photoelectric measuring means.

Several choices of geometry can be made for measuring the light scattered by a material. Some designs involve reverse scattered light (*1*), some scattering at right angles to incidence (*6*, *10*, *11*), some at selected angles (*5*), and some in transmission (*3*, *7*, *12*). Two of the latter include the accompanying change in transmission as part of the measurement (*7*, *12*). The present instrument falls into the class wherein forward scattering alone is measured. However, it differs from other instruments in that instead of measuring within a small selected solid angle the forward scattering within almost the complete hemisphere is integrated. This procedure illuminates the sensitive surface of the barrier layer photocells diffusely and thus avoids the complication, introduced under direct illumination, of the variation in sensitivity of different parts of the sensitive surface.

The sphere turbidimeter was devised as the result of a need for an instrument combining simplicity of construction and operation with reliability of readings approaching that of a null method (*4*). These were achieved by comparing the total flux transmitted by the specimen with that portion scattered during the transmission, thus making each specimen in essence its own standard and thereby also substantially eliminating the problem of color compensation. A similar procedure has been described by Kortschak (*6*). The rapidity with which the two readings can be taken merely by opening the exit hole makes it unnecessary to consider fatigue of the cells or any except rapid changes in the material being measured.

The ability to discard substantially all unscattered light, to introduce a known correction for the remainder, and to measure substantially all of that scattered into the sphere, provides a simple ratio relationship of the two quantities. The small numerator (scattered light) is obtained with much better precision by this direct means than if it were calculated arithmetically as the difference between two large numbers, such as total flux minus unscattered transmission.

Operation to obtain a measurement involves only insertion of the specimen, reading a galvanometer deflection, D_1, at a certain shunt factor, S_1, with the exit hole closed, then opening the flap to obtain a reduced brightness in the sphere, corresponding to a second galvanometer deflection, D_2, usually at a higher sensitivity shunt setting, S_2. The turbidity is then defined in per cent as

$$T = 100\,\frac{D_2S_1}{D_1S_2} - T_i \tag{1}$$

where T_i is the instrument error previously determined, for the instrument alone in the case of solids, or for the instrument plus cell where liquids are measured.

MEASUREMENT OF POWDER SUSPENSIONS

When in 1940 it became necessary in this laboratory to determine the relative specific surface of highway cements, consideration was given to the relative merits of the sphere turbidimeter as compared with those of A.S.T.M. Method C115 (*2*). Experimentation with the former demonstrated that turbidity readings of known concentrations suspended in kerosene were linear with concentration up to a turbidity of about 50%. Furthermore, by making use of sharply separated fractions of cement, which had been "infrasized" (separation by entrainment in air moving vertically upward through cylinders of increasing diameters) and checked by microscopic examination, a simple relationship was experimentally established between turbidity and particle size (Figure 3). By means of these relationships and a few simplifying assumptions it was possible to show by a mathematical approach that the relative specific surface of cement (and probably also of other powders approximating ellipsoids wherein the three principal axes are of the same order of magnitude) consisting of any distribution of particle size could be obtained by a single pair of readings: (1) the total transmission and (2) the fraction of light scattered during the transmission.

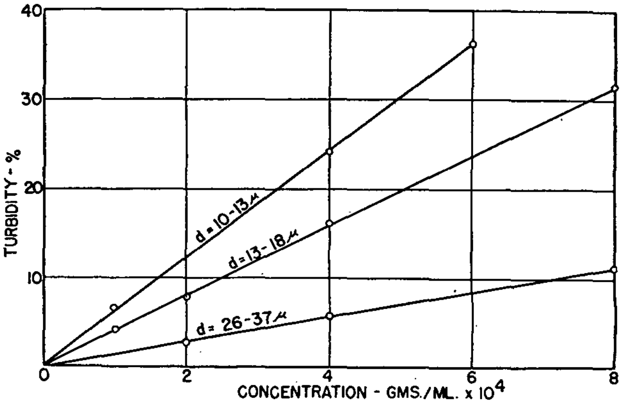

Figure 3. Relation of Particle Size and Concentration of Portland Cement in Kerosene to Turbidity

Thickness of glass cell, 1.0 cm.

By inserting the per cent turbidity from Equation 1 into either of two empirical formulas, a figure for either relative specific surface, S, or average particle diameter (calculated on the assumption of spherical particles. These quantities will therefore be proportional to the absolute specific surface and linear dimension of nonspherical powders) with respect to surface, d_s, can be calculated,

$$S = \frac{6}{\rho}\left[\frac{T}{kc}\right]^{\beta} \tag{2}$$

$$d_s = \left[\frac{T}{kc}\right]^{-\beta} \tag{3}$$

where c is concentration, ρ is density, and β and k are constants depending on instrument geometry and particle shape but not on the color of either of the phases. For the cement measured, $\beta = 0.689$ and $k = 3.30$, giving the relationship between S in square centimeters per gram and T in per cent, described by

$$S = 1.905\ [606\ T]^{0.689} \qquad (4)$$

when $\rho = 3.15$ grams per cc. (usual for cement) and $c = 5 \times 10^{-4}$ grams per ml. This is shown graphically in Figure 4.

MEASUREMENT OF HAZINESS OF PLASTICS

The problem of residual haze in ostensibly transparent plastics is one that has long required a reliable means of evaluation, both as an aid in the development of clearer materials and for the equitable establishment of quality specifications. Realizing this, the optical subcommittee of A.S.T.M. Committee D-20 on plastics has for a number of years been active in evaluating apparatus and techniques for making these measurements.

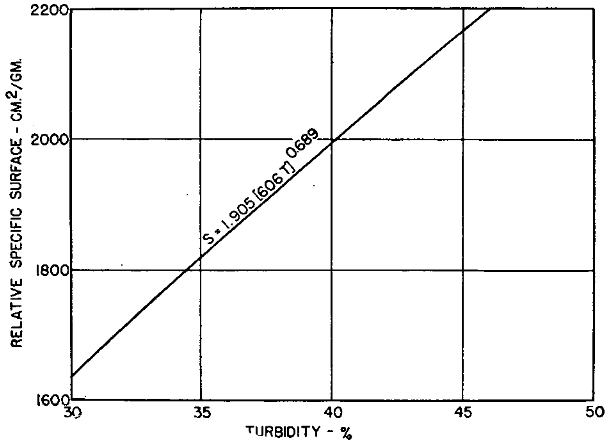

Figure 4. Relation of Turbidity to Relative Specific Surface of Portland Cement

1.0-cm. glass cell at concentration of 0.0005 gram per ml.

Where the haze has been sufficiently pronounced, a suitable method is available (*3*). However, the differentiation of low values has been a more difficult problem. When the attributes of the sphere turbidimeter were brought to the attention of this group a number of years ago, a study of its capabilities was undertaken and is continuing. This work was actively prosecuted under the able direction first, of R. F. Clash, Bakelite Corporation, and later, of G. W. Ingles, Monsanto Chemical Company. It has resulted in the construction, by a number of laboratories, of modifications of this instrument so arranged as to be particularly suited for measuring specimens of plastic sheet. Several interlaboratory comparisons of standard samples have been carried out. Differences in data obtained for these have resulted in detection and elimination of sources of error arising from constructional differences. Although according to the latest such data (Table I) additional work appears necessary, particularly in preparing satisfactory permanent specimens, the technique still seems to hold considerable promise.

The general operating procedure of the sphere turbidimeter has also been adapted by this subcommittee for use in conjunction with recording spectrophotometers (similar to those manufactured by the General Electric Company). Because of the expense of this instrument, however, it is intended to be used only in a referee method capable of greater precision. Both projects are being carried out in parallel. Latest data kindly supplied by the subcommittee are summarized in Table I.

Examination of Table I shows that in many instances the variation obtained in repeated tests with the same instrument (column F) is of the same order of magnitude as that shown among various turbidimeters (column D). As the precision of the instrument is limited only by that of the Ayrton shunt and the scale of the box galvanometer, it can be maintained at about 1 to 2% of the reading, limited for lower turbidity values by its sensitivity (ca. 0.5% for 2% precision). It hence appears that a major difficulty consists in preparing plastic-in-glass specimens of the low light-scattering characteristics shown, which will be satisfactorily uniform over their surface.

In spite of the somewhat different geometry of the spectrophotometer as contrasted with the turbidimeter, Table I appears to indicate that further work by the A.S.T.M. group may well result in as good agreement between the types of instruments as among those of the sphere turbidimeter.

CLARITY OF LIQUIDS

In the control of quality of beer one aspect concerns the clarity of the brew as affected by several steps in the process of manufacture. Description of the sphere turbidimeter to J. W. McBain resulted in his constructing an instrument with which he was later successful in examining the turbidity and obtaining an empirical color index for various beers sampled from the retail market, as well as at various stages during manufacture (*9*).

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance obtained from E. F. Champaygne, who constructed the turbidimeter, as well as to thank others who from time to time contributed to this work.

Table I. Haziness of Eleven Standard Samples, Measured by Recording Spectrophotometer and by Sphere Hazemeter[a]

Sample No.	A. Haze by Spectrophotometer %	B. Range[b] %	C. Haze by Sphere Hazemeter %	D. Range[b] %	E. C − A	F. Variation in Repeated Measurements on One Hazemeter, Range %
1	1.0	±20	1.0	±20	0.0	±19
2	1.4	±7	1.6	±6	+0.2	..
3	2.0	±15	2.0	±10	0.0	±16
4	2.0	±15	2.4	±3	+0.4	±6
5	2.3	±30	4.4	±57	+2.1	±40
6	4.5	±7	4.5	±9	0.0	±5
7	6.7	±4	8.4	±21	+1.7	±13
8	9.0	±9	9.4	±10	+0.4	±3
9	11.0	±5	11.1	±9	+0.1	±3
10	16.8	±5	16.9	±4	+0.1	±1
11	28.7	±4	29.0	±4	+0.3	±3

[a] Averages for four instruments of each kind.
[b] Range within which a single value falls with probability of 0.9.

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SURFACE CHROMATOGRAPHY

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A powdered adsorbent, fixed rigidly to a microscope slide by means of a suitable binder, provides a convenient system for microchromatography. By means of a flexible technique and sundry variations in method, the system demonstrates broad applicability. Its use is illustrated in the analysis of a simple mixture of iron (III) and zinc salts.

IZMAILOV and Shraïber (*6*) chromatographed organic mixtures on thin layers of adsorbent powders, and observed the resulting concentric circular zones under ultraviolet light. Williams (*10*) developed the idea further by forming a sandwich of adsorbent between glass plates, the upper plate containing a small hole through which solutions are introduced. These methods suffer from the disadvantages inherent in working with loose powders. Hopf (*5*) demonstrated the use of filter papers impregnated with complexing agents for the chromatography of metallic ions. Brown (*2*) employed a sandwich of blotting paper, a device like that of Williams, in the analysis of organic mixtures. These methods suffer from the limited choice of adsorbent compositions, and from discontinuities and variations in the adsorbing medium. The system described below was developed with the hope of eliminating the faults and combining the virtues of the foregoing methods.

In the chromatography of inorganic compounds the adsorbent of choice appears to be alumina, but considerable variations in average particle size and in particle size distribution exist among commercial products. It is advisable, therefore, to hold to a single product and, where possible, a single batch. In this research Merck's reagent aluminum oxide was successfully employed and was used directly without activation treatment. A number of preliminary tests showed that average particle size was a much more important factor than any type of activation treatment.

In order to fix the adsorbent in a continuous, rigid surface, a binder must be used. Among several adhesives tested, ordinary cornstarch was found to be one of the best. Most resinous materials—e.g., glyptal, phenol-formadehyde, etc.—were disqualified on the basis of their color-forming and hydrophobic properties. A brief survey of various starches led to the adoption of Amioca starch (National Starch Products Co.). Amioca, consisting mainly of amylopectin, contributes to the ease of compounding through its comparatively sharp gelatinizing range (70° to 80° C.). The tendency toward skin formation and the occurrence of lumps observed in formulations employing ordinary starches are considerably reduced when Amioca is substituted.

An analytical filter aid, Celite (Johns-Manville), is added to improve rigidity and to prevent fissuring in the final surface. The ingredients are slurried with water, heat coagulated, triturated to a sirupy consistency, plated on microscope slides, and dried.

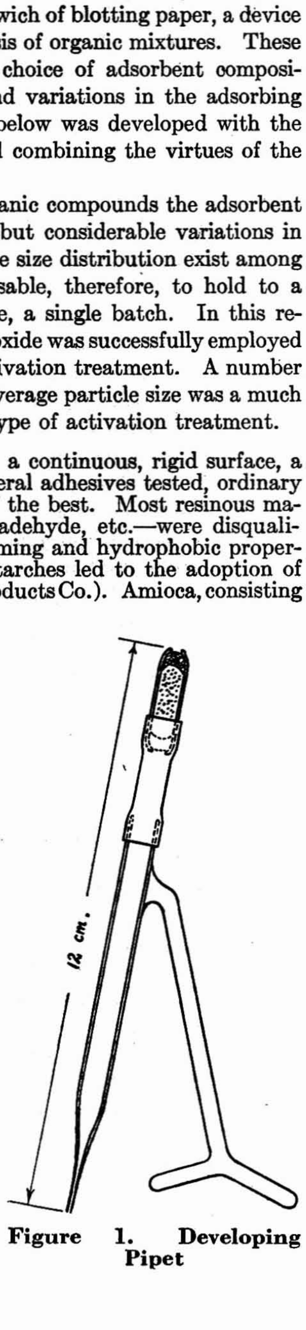

Figure 1. Developing Pipet

PROCEDURE

Three and one half grams of Celite (35% dry basis), 0.3 grams of Amioca, and 6.2 grams of alumina are thoroughly mixed (dry), then slurried with 18 ml. of distilled water. The mixture is warmed, with agitation, on a water bath until coagulation is complete. The coagulum is allowed to cool, then triturated with an additional portion of water (2.5 ml.) until a thick cream is formed. The product is applied to microscope slides by means of a spatula and spread evenly to a depth of 2 mm. Gentle tapping of the slide ensures even distribution and a smooth surface. One end of the slide is left untreated in order to facilitate handling. The microscope slides require no previous treatment except cleaning to prevent the presence of an oil film. The freshly prepared slides are dried in a dust-free atmosphere, either at room temperature or at 90° C. A somewhat more even surface is obtained with slow drying. The quantities given above are sufficient for treating 12 to 13 slides.

The surface thus obtained possesses mechanical stability and a fine, even texture. It exhibits no tendency toward deformation when wetted with aqueous or organic liquids.

METHOD

The chromatographic process may be divided into four general parts: (1) application of sample; (2) development with solvent or reagent; (3) immobilization of adsorbate; and (4) introduction of a color reaction, or a physical process, which differentiates between the zones formed. In their work on the chromatography of inorganic ions Schwab and Jockers have, unfortunately, applied the term development to part 4, which is at variance with general usage and introduces an ambiguity (*9*). In this report the second phase of the process is called development, while the fourth phase is referred to as ripening.

The sample is prepared according to the type of separation desired. This will depend on the specific equilibria involved. Inasmuch as this procedure involves a dilution of the solute, fractionation may be based on the relative rates of decomposition (or solvolysis) of metal complexes to an insoluble, or less mobile, species. In other cases fractionation may depend on the precipitation of hydrous metal oxides, or oxy- salts, under the influence of a gradual increase in pH. Here it is required merely that the original sample be sufficiently acid to hold all ions in solution.

The sample is introduced into the surface by means of a capillary pipet of 0.005- to 0.008-ml. capacity. The pipet is a simplification of one originally described by Harkins and Anderson (*4*) and consists of a section of drawn capillary tubing 5 cm. long sealed into the end of a section of ordinary glass tubing by means of a thermoplastic resin. The pipet is filled by capillary action, or by gentle suction, and is drained into the adsorbent surface by capillary action.

Development is carried out with water, or other reagent, using a pipet designed according to Figure 1. It is a modified medicine dropper with a support of glass rod sealed to its side. Instead of the usual rubber bulb, a short section of rubber tubing is used for filling, and its upper end is stoppered with a short column of firmly packed alumina. This arrangement allows drainage of the liquid at a slow steady rate. The delivery end of the pipet is drawn to capillary dimensions. The filled pipet is applied to the slide at the point of introduction of the sample. Development is carried out until the wet circular area approaches the edges of the slide. A slight further spreading takes place after removal of the pipet.

Ripening may now be carried out on the still moist latent pattern by the application of gaseous reagents—e.g., ammonia, hydrogen sulfide, iodine. When iodine vapor is used, reaction occurs with the starch binder. The blue color is profoundly influenced by the presence of certain ions, and thus reveals their location. The pattern formed, however, is not stable, because zone boundaries gradually diffuse and become indistinct. For this reason an immobilizing or fixing operation is introduced (part 3). The hydrous oxides of the metals may be precipitated with ammonia gas, or the slide may be dried. The most even patterns result from slow drying. An oven temperature of 50° C. is recommended.

Typical chromatographic slides are presented in Figure 2. These examples were taken at random from a large number of tests and are included here primarily to demonstrate the type of patterns obtained rather than for any special significance they may have. All these slides were ripened with iodine vapor.

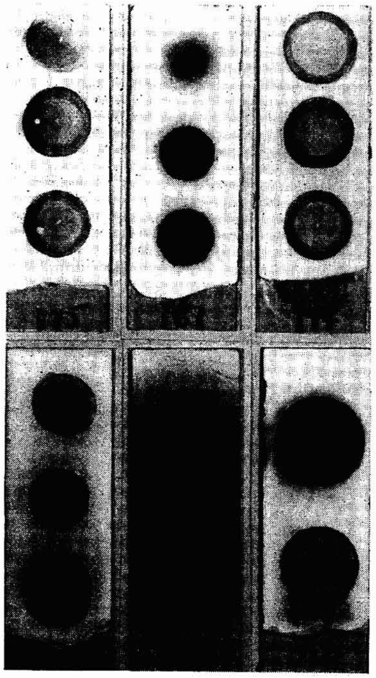

Figure 2. Iodine-Ripened Chromatograms

No. 194 (lower middle) is overripened, while No. 175 (upper left) is unevenly ripened. In these patterns samples of pure beryllium nitrate (0.5 molar) are compared with samples contaminated with traces of iron and aluminum. No. 155 (lower left) was developed with dilute hydrochloric acid; the two lower patterns of No. 167 (upper middle) were developed with glacial acetic acid and the upper pattern with methyl isobutyl ketone. Nos. 174 and 175 (upper left and right) were developed with 50 and 25% acetic acid, respectively. No. 264 (lower right) was developed with the mixture: acetic acid 5%–ethylene glycol monoethyl ether 15%–water 80%. In all cases pure beryllium nitrate gave sharper patterns than the impure samples. This is best indicated in the middle patterns of Nos. 175 and 174, and in the bottom pattern of No. 264. The developing time for No. 264 was 8 minutes. The light colored zones in these chromatograms are not "empty" zones, but lighter shades of buff, blue, or violet. They indicate composition gradients of both developer and original solute. In no cases were metal zones found to be separated by unoccupied zones.

A number of different methods of ripening have been employed in this work. The application of iodine vapor is sometimes erratic and difficult to control. To a dried slide, iodine is best applied in a carbon tetrachloride solution (0.85 gram of iodine per liter) using a medicine dropper. The excess solution is drained off and the slide allowed to dry briefly. This is followed by gentle humidification which brings out the pattern in sharp relief. This technique has proved exceedingly useful and reliable.

This type of ripening is an example of a general method which employs a color reaction not directly involving the chromatographed ions. Although the ions themselves form no colored product, their presence influences the course of the reaction and becomes manifest in a change of shade or intensity of color. This type is further exemplified in the work of Brockmann and Volpers (*1*) and of Sease (*8*), who chromatographed organic mixtures on fluorescent adsorbents—e.g., alumina treated with small amounts of heavy metal, etc.—and located the adsorbates by differences in fluorescence of the irradiated column.

A second type of ripening is adapted from the differential staining techniques employed in bacteriology. The freshly developed chromatogram is treated with ammonia gas, or other suitable reagent, to form an insoluble, highly adsorbent structure with the metal salts present. Indeed, the original developing process itself may be sufficient to form this kind of structure. The slide is then treated with a dye solution, followed by gentle washing with an aqueous detergent solution. The detergent differentially desorbs the dye. Obviously, a too highly activated alumina, or a too readily adsorbed dye, will give rise to irreversible adsorption throughout the whole system. As the alumina used in this work has been ignited to at least 900° C. during manufacture (according to density measurements), its adsorbing characteristics are sufficiently different from the hydrous metal oxides to allow differential staining.

This was illustrated in the chromatography of iron (III) and zinc ions (0.25 molar in each ion) when a 0.1 *N* hydrochloric acid developer was used. The moist slide was treated with ammonia gas, followed by a solution of methylene blue, then gently agitated in a warm solution of sodium stearate. The zinc zone retained its deep blue stain, while the iron zone gave up the dye completely and retained only its original brown color. The alumina remained a pale blue which did not interfere with the sharp definition of the zinc zone.

A third type of ripening consists of applying colorimetric reagents directly to the adsorbed species. A number of methods of application have been used. Nickel, for example, is readily located by pressing against the surface a filter paper saturated with dimethylglyoxime solution. Instead of filter paper, an atomizer may be used to give a more even application. Masks may be employed which allow only a given sector of the pattern to be treated at one time, and thus make it possible to use several reagents on one chromatogram. If a reagent is volatile with heat, a previously saturated and dried filter paper may be pressed against the chromatogram by a hot metal surface—e.g., a knife blade. 8-Hydroxyquinoline has been applied in this manner to locate iron. It is necessary to have the iron in an ionic state, and the slide must be previously humidified and treated with hydrogen chloride vapor.

Fourth, the ripening process may form an integral part of the development. In this method a complexing agent—e.g., 8-hydroxyquinoline—is included in the adsorbent composition. Erlenmeyer and Dahn (*3*) have demonstrated its use in column chromatography. There are certain inherent disadvantages in this method. The surface is limited in its use to those metals which form colored complexes; some of the complexing agent migrates during development; the surface characteristics of the adsorbent do not remain constant. Considerable difficulty was experienced in obtaining reproducible results in this medium.

Finally, sulfur may be incorporated in the adsorbent surface. The dried chromatogram is exposed to infrared radiation (or heated in an oven), revealing those metals which form colored sulfides. Iron, for example, appears as a red-brown zone which gradually turns black. This type of treatment also has limitations but appears to be highly selective in certain cases.

FILING

When desired, chromatograms may be filed for future reference in much the same way as specimen slides. The adsorbent surface may be marked with a pencil, and a protective transparent coating may be applied. Slides developed with iodine have a tendency to fade slightly over a period of time but may be reripened. A more convenient method of filing is as follows:

The adsorbent surface is first softened by humidification. Then a short section of transparent Scotch tape is pressed firmly on the desired chromatogram, while the ends are left free. When the tape is withdrawn the pattern adheres to it, and with the free ends it may be pasted into a notebook.

MEASUREMENT

Ring radii were measured with a vernier caliper, graduated in 0.001 inch, and mounted horizontally above the slide. Attached to the underside of the vernier was a glass slide with ruled cross hairs which cleared the adsorbent surface by 1 mm. Readings were taken by aligning the perpendicular cross hair tangent to a circular zone boundary at the point of intersection of the cross hairs. The chromatogram was rotated through 360° in order to take readings in all sectors.

Calculations were made according to the equation given by Hopf (*5*),

$$\frac{c_a}{c_b} = \frac{r_2^2 - r_1^2}{r_3^2 - r_2^2} K_{a/b} \qquad (1)$$

where c_a and c_b are the concentrations of ions a and b, respectively, in the original solution, $K_{a/b}$ is a proportionality constant, and $r_3 > r_2 > r_1$. This equation is based upon the assumption that the ratio of the concentrations of the ions in the sample is proportional to the ratio of the respective zone areas obtained. r_2 in this equation is the outer radius of one zone and the inner radius of the next adjacent zone. Metal zones were never found separated by blank zones.

Table I. Development with 0.04 *N* Hydrochloric Acid

r_1	r_2	r_3	K	d
225	291	352	1.15	0.10
227	291	350	1.14	0.11
222	285	346	1.21	0.04
216	280	345	1.28	0.03
215	276	344	1.41	0.13
234	299	358	1.12	0.13
230	297	366	1.30	0.05
235	295	364	1.43	0.18
236	296	359	1.29	0.05
234	292	356	1.36	0.11

$K(av) = 1.25 \pm 0.092$; average deviation = 7.4%.

RESULTS WITH SPECIFIC IONS

Iron (III) and zinc ions were selected for initial experiments, because these elements are readily separated and easily located. A solution of the chlorides was used, 0.25 *M* in each metal, and acidified sufficiently to maintain the iron in a sensibly ionic state. The sample was introduced into the surface by means of the capillary pipet described above. Development was carried out with various liquids by means of the developing pipet. The slide was dried, either at room temperature or in an oven, treated with iodine in carbon tetrachloride, and humidified. The resulting chromatogram consisted of a central hydrogen-ion circular zone (white to pale pink) followed by an iron-ion zone (straw colored), a zinc-ion zone (pale to intense blue), and finally a peripheral zone (amber to deep violet). The interpretation of these patterns was clearly established by chromatography of these ions singly and by testing with colorimetric reagents—e.g., 8-hydroxyquinoline. It is believed that the peripheral zone contained starch degradation products (from the catalytic effects of the alumina during the cooking process) plus a small component of displaced alkali metal ions. These zones possessed sufficient color contrast and boundary sharpness to permit easy measurement.

Table II. Zn/Fe Solution Developed with Hydrochloric Acid

Concn. of Developer, *N*	$K(av)$	% $d(av)$
H_2O	1.72	6.6
0.04	1.25	7.4
	1.18	13.8
0.06	1.69	16.1
	1.71	12.0
0.1	1.01	9.6
	1.03	7.9
	1.16	7.7
	1.08	13.7
	1.25	8.3
0.2	0.634	10.2
	1.28	13.1
0.3	0.348	19.3
	0.874	8.3
	0.645	17.2

In Table I are presented the zone radii measurements of a single typical chromatogram (inches × 10^{-3}). r_1 represents the inner radius of the iron zone, r_2, the outer radius of the iron zone (inner radius of the zinc zone), and r_3, the outer radius of the zinc zone. *K* (Equation 1) is computed for each set of measurements, and *d* is the deviation from $K(av)$. Varying concentrations of hydrochloric acid were used as developer, as indicated in Table II. Each $K(av)$ is the average of ten sets of measurements, the corresponding average deviation being recorded in the third column.

Preliminary studies have been made on mixtures of a number of other metallic ions, but it is too early to draw definite conclusions from this work.

DISCUSSION

It will be seen from Table II that *K* decreases as the concentration of the acid increases, and that the concentration region of greatest precision is 0.1 *N*. A discussion of the theoretical aspects of this problem is beyond the scope of the present paper, but it should be pointed out that the fundamental process taking place is not, as has been previously suggested (*7*), primarily one of ion exchange. In an ion-exchange process *K* would remain essentially constant for small changes in the developer concentration, as the ratio of the ion zone areas would be equal to the ratio of the milliequivalents of the ionic species present in the chromatogram. Such is not the case in the present situation. Furthermore, the quantity of ions in the original sample far exceeds the exchange capacity of the adsorbent.

Neither does the process appear to depend upon the adsorption of the ionic species. This is indicated by the experimental observation that the usual activation treatments have little effect on the final pattern. On the other hand, both the particle size of the alumina and the pH of the developer have a profound influence on the patterns obtained. Some brands of alumina, unsuitable for use in this method of chromatrography, could not be improved by any ordinary activation treatment. Careful hydraulic classification of these same materials yielded a much more effective adsorbent.

Again, ionic mobilities as determined by transference methods do not appear to be a controlling factor.

The separation appears to depend, rather, on the relative rates of formation of the insoluble hydrous metal oxides through a gradual increase in pH. The insoluble material is less mobile than the ionic species and is retained in the interstices, or free space, of the adsorbing medium. Because iron hydrolyzes at a lower pH than zinc, it is deposited first. Development, then, may be considered a dilution process. In the general case, a set of competing equilibria is selected, depending on the chemical properties of the ions in question, and made the basis of a fractionation.

A number of other factors, such as variations in the geometry of the adsorbent bed, channel size and shape, rate of development, etc., also influence the process but are maintained as nearly constant as possible. Obviously much work needs yet to be done before this method can become a dependable analytical tool, and work is being continued on other ions and on improvements in technique. It promises, however, to become not only a rapid routine micromethod, but also a means of exploring fractionation processes to be later developed on a macro scale.

ACKNOWLEDGMENT

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Determination of Bismuth in Biological Material

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Bismuth is extracted from biological materials in the presence of acetic acid at pH 2.5 by successive portions of dithizone in carbon tetrachloride. Extraction is quantitative and phosphates and halides do not interfere.

THE use of dithizone for the determination of bismuth in biological material has been attended by certain difficulties, chief of which is the presence of interfering anions which form complexes with bismuth. Hubbard (*2*) has proposed the separation of bismuth from extraneous salts by a sulfiding procedure preliminary to determination with dithizone. This method is rather long. Recently (*1*) Hubbard presented a simplified method in which the direct extraction of bismuth with dithizone is effected in the presence of ammonium citrate in dilute alkaline solution. This method, while apparently satisfactory for urine and blood, is difficult to apply to biological materials high in phosphates. The following method which utilizes a newly discovered principle for the separation of bismuth from interfering salts, has had extensive application to a variety of biological materials.

PRINCIPLE

The fact that bismuth can be extracted with dithizone from aqueous solutions at pH 2 is the basis for the separation of bismuth from lead, but attempts to apply this procedure to the direct extraction of bismuth from acidified digests of biological materials have met with failure because of the serious interference of halides and phosphates. However, in the presence of 20% acetic acid, and if carbon tetrachloride is substituted for chloroform as the solvent for dithizone, quantitative extraction of bismuth may be made in the presence of phosphates and halides at pH 2.5. Simultaneously a separation from lead is effected.

REAGENTS

Dithizone (diphenylthiocarbazone). The reagent commercially available is now suitable for use without further purification.

Carbon Tetrachloride and Chloroform. Use of analytical reagent grade quality supplied in glass containers is recommended. Recovery of used solvents and purification by distillation of inferior grades is not recommended.

Solutions of Dithizone. 7 mg. per liter of chloroform and 100 mg. per liter of carbon tetrachloride. It is preferable to make up these solutions by weighing out the dithizone directly rather than by diluting from concentrated stock solutions.

Nitric Acid, analytical reagent grade. A 0.2% nitric acid is prepared in 20-liter lots by diluting the reagent grade with glass-distilled water. The dilute acid should be stored in Pyrex bottles.

Glacial Acetic Acid, analytical reagent grade.

Ammonium Hydroxide, analytical reagent grade, redistilled and stored in paraffin-lined bottles. Approximate titer 14 *N*.

Potassium Cyanide, analytical reagent grade. Certain grades of cyanide have been shown to contain sufficient traces of sulfides to give a distinct darkening when tested with lead acetate. Sulfide interference may be far more serious than heavy metal contamination. The best analytical reagent grade is therefore recommended, and this should be tested for sulfides before any attempt is made to remove heavy metals either by dithizone (*2*) or by the flocculation procedure with calcium chloride as used in this laboratory (*3*).

Ammonia-Cyanide Solution. This is prepared by dissolving 25 grams of potassium cyanide and 40 ml. of 14 *N* ammonium hydroxide in 1 liter of glass-distilled water. Storage should be in paraffin-lined bottles.

Potassium Bromide, analytical reagent grade. Precautionary tests should be made to ensure a reagent free from sulfides. Removal of lead is easily effected with dithizone (*4*). As used in 40% w/v concentration, the solution should be maintained slightly alkaline by the addition of a drop of 2 *N* sodium hydroxide.

Sodium Hydroxide, analytical reagent grade, 2 *N* solution.

Thymol Blue Indicator, 0.04% solution.

METHOD IN BRIEF

Samples containing bismuth are dry-ashed at 500° C. in a muffle and dissolved in concentrated nitric acid. To the total ash solution or a suitable aliquot, somewhat diluted with water, glacial acetic acid is added and the pH is adjusted to 2.5. Bismuth is extracted with successive portions of dithizone in carbon tetrachloride. Under these conditions no lead is extracted, but some copper and zinc are. The metal dithizonates are washed with dilute nitric acid and then with dilute nitric acid containing potassium bromide. By this means, bismuth dithizonate is decomposed and the bismuth reverts to the aqueous phase as a complex bromide salt. When the aqueous phase is adjusted to pH 9.5, this complex is again decomposed. Bismuth is then extracted with dithizone in chloroform and the density of the colored solution is determined in a spectrophotometer at 490 mμ.

Procedure. Place the ash solution (2 ml. of concentrated nitric acid are usually sufficient to dissolve the ash from 10 grams of soft tissue), estimated to contain not more than 10 micrograms of bismuth in a 250-ml. Squibb-type Pyrex separatory funnel. Add

10 ml. of glacial acetic acid and bring the volume to approximately 50 ml. with water. Add 5 drops of 0.04% thymol blue and adjust the pH to 2.5 (distinct yellow) with 2 *N* sodium hydroxide. The solution must be cool at all times. Extract the bismuth with successive 10-ml. portions of dithizone in carbon tetrachloride (100 mg. per liter). The last extract should appear green. Combine the carbon tetrachloride extracts in a second funnel and wash by shaking vigorously 100 times with 50 ml. of 0.2% nitric acid.

Transfer the washed carbon tetrachloride solution of the dithizonates to a third funnel, making sure that any remaining droplets in the second funnel are included, by flushing with a few milliliters of carbon tetrachloride. To the third funnel add 50 ml. of 0.2% nitric acid and 5 ml. of 40% w/v potassium bromide; shake vigorously 100 times. Discard the dithizone solution and wash the aqueous phase with 5 ml. of carbon tetrachloride. Discard the wash solution and carefully free the aqueous phase as completely as possible from droplets of carbon tetrachloride. Add 5 ml. of the ammonia-cyanide solution, which adjusts the pH to 9.5. Add exactly 10 ml. of dithizone solution in chloroform (7 mg. per liter) and shake vigorously 100 times. Filter the chloroform solution of bismuth dithizonate through a pledget of metal-free cotton inserted in the stem of the funnel, discarding the first milliliter which comes through. Measure the density of the dye at 490 mμ in a suitable spectrophotometer.

NOTES AND COMMENTS ON METHOD

Chloride Interference. At a pH of 2.5 the presence of 20% acetic acid and the use of a strong solution of dithizone in carbon tetrachloride effectively prevent the complexing action on bismuth of moderate amounts of chlorides (up to 1 gram). Below a pH of 2, however, chlorides will interfere, even in the presence of large amounts of acetic acid. It is therefore essential that the adjustment of the pH be kept close to 2.5. Because excessive amounts of hydrochloric acid are frequently used in routine work to effect the solution of the ash, a safer procedure seems to be the use of nitric acid for this purpose, in spite of the fact that this acid is generally considered to be a poorer solvent. No interference with chlorides was observed when a sample of ash was dissolved in 2 ml. of 6 *N* hydrochloric acid and used in toto.

Phosphate Interference. At a pH of 2.5 no precipitation of magnesium and calcium phosphates occurs. Furthermore, relatively large quantities of phosphate (up to 1 gram) do not prevent the extraction of bismuth by any complexing reaction. Thus the analyses of bone samples present no difficulty. As in the case of the chlorides, however, reduction of the pH below 2 causes marked complexing effects; hence similar precautions are necessary. In cases where appreciable quantities of iron and phosphate are present (blood or liver ash) ferric phosphate may slowly precipitate. This first appears as a fine haze, which is intensified if the solution has become warmed from the neutralization to pH 2.5. It is therefore recommended that extraction with dithizone be made immediately after adjustment of the pH. If, after the first extraction, a slight haze does form, the solution should be reacidified in order to dissolve the ferric phosphate. After readjustment to pH 2.5, extraction with dithizone may be repeated. Complete recoveries of added bismuth could be made under these conditions, but losses of the order of 10% occurred if this precaution was not followed.

Table I. Recovery of Bismuth Added to Rat Tissues[a]

Tissue	Wet Weight	Bismuth Added	Bismuth Recovered
	Grams	*Micrograms*	*Micrograms*
Liver	12.4	25.0	24.5
	11.2	25.0	26.4
	7.9	10.0	10.4
	10.5	9.00	8.70
Kidney	1.6	10.0	9.62
	3.0	9.00	8.92
	2.2	3.00	3.21
Spleen	0.42	5.00	5.00
Heart	0.89	5.00	5.48
Lung	2.1	7.50	7.60
Skin	2.6	5.00	4.96
Muscle	4.0	10.0	10.3
	3.1	9.00	9.00
	3.4	10.0	10.1
Bone	1.2	50.0	50.0
	2.4	50.0	48.9
	0.63	9.00	9.00
	1.0	10.0	9.40
Brain	2.0	7.50	7.54
	1.6	9.00	9.00
	1.8	10.0	10.1
Blood	8.7	9.00	8.00
	4.4	10.0	9.77
	7.5	3.00	3.14

[a] No bismuth was ever found in control tissues from which bismuth had been excluded.

Extraction of Other Metals. At a pH of 2.5, in the presence of acetic acid, carbon tetrachloride solutions of dithizone will also extract some zinc and considerable quantities of copper. There appears to be competition of the metals for the dithizone, with copper taking precedence. It is necessary to continue the treatment with dithizone until no more metal is extracted; otherwise losses in the recovery of bismuth will occur.

Washing with 50 Ml. of 0.2% Nitric Acid. It is necessary to wash the carbon tetrachloride solution of the dithizonates of copper, bismuth, and zinc because acetic acid is appreciably soluble in carbon tetrachloride. Thus, if this step were omitted, sufficient quantities of acetic acid would be carried over into the final aqueous phase and produce large fluctuations in the pH at which the bismuth is extracted. The final pH of 9.5 must be fixed; otherwise variable amounts of dithizone will dissolve in the aqueous phase. The fact that the wash with 0.2% nitric acid causes zinc to revert to the aqueous phase is merely coincidental. Separation of bismuth from zinc would be effected upon treating the final solution with cyanide.

Reversion of Bismuth to the Aqueous Phase with Potassium Bromide in 0.2% Nitric Acid. Considerably stronger nitric acid than 0.2% would be necessary to "strip" the bismuth dithizonate into the aqueous phase. However, in the presence of potassium bromide this becomes very easy because a complex bromide is formed, similar to that formed with mercury (*4*). The separation of copper by this process is coincidental and of no importance, as the final solution is treated with cyanide. When the solution is made alkaline, the bismuth-bromide complex is destroyed, and bismuth may then be again extracted with dithizone.

Standards. For the purposes for which this method was developed, a working standard range from 0 to 10 micrograms of bismuth was found most convenient. Standard curves were set up by carrying through the entire process (except for ashing)—i.e., 0, 2.5, 5.0, 7.5, and 10.0 micrograms of bismuth were added to the first row of extraction funnels in the presence of 2 ml. of concentrated nitric acid and neutralized and extracted as in the case of unknowns. The spectrophotometer tubes were 5 cm. long and of all-glass construction. Other bismuth ranges to suit the convenience of the investigator are feasible and may be effected by varying the volume and/or concentration of the final dithizone solution and the length of the spectrophotometer tubes.

Blank. No bismuth was found in any of the analytical reagents used. Purification of reagents such as potassium cyanide, ammonium hydroxide, and potassium bromide which are present at the final extraction of bismuth is desirable in order to exclude lead, a frequent contaminant.

RESULTS

In Table I are listed the results of recovery experiments in which bismuth was added to a number of rat tissues.

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NOTES ON ANALYTICAL PROCEDURES . . . .

Indirect Method for Estimation of Sodium in Water Supplies

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GUSTAFSON and Behrman (*1*) describe a simple method for calculating the noncarbonate solids in natural waters from determinations of the alkalinity and conductance.

Table I. Sodium in Water

No.	1	2	3	4	5	6	7	8	9	10
				P.P.M. as $CaCO_3$						
Calcium	25.1	111	25	687	27.7	19	97	193	5	57
Magnesium	31.7	110	575	400	12.7	5	49	65	4	37
Sodium	0	7	52	117	12.4	12	119	389	17	396
Bicarbonate	31.7	168	617	244	10.1	28	160	254	5	214
Sulfate	25.1	33	18	954	5.0	3	25	52	1	1
Chloride	0	24	17	6	37.7	5	68	340	4	275
Nitrate	0	3	0	0	0	0	12	1	16	0
Alkalinity	31.7	168	617	244	10.1	28	160	254	5	214
Hardness	56.8	221	600	1087	40.4	24	146	258	9	94
				Micromhos at 25° C.						
K	119	452	1100	....	127	72	523	1345	53	1020
K_d	...	471	1228	2780	...	..	558	1495	..	1087
				Per Cent Sodium						
Analysis	0.0	3.1	8.0	9.7	23.5	33.3	44.9	60.1	65.4	80.8
Equation 2	−1.17	4.6	7.4	8.1	24.9	33.3	44.9	61.3	60.2	80.9

Using the same method, it is possible to compute the sodium concentration with fair accuracy when the alkalinity, hardness, and diluted conductance are known. The alkalinity and hardness may be rapidly determined by titrimetry, and the diluted conductance is determined by diluting the water sample with cool boiled distilled water so that the specific conductance is approximately 100 micromhos at 25° C. This value, multiplied by the dilution factor, is the diluted conductance. Sodium is then found from the equation:

$$\text{Sodium (p.p.m.)} = 0.186\,K_d + 0.113\,(\text{alkalinity}) - 0.46\,(\text{hardness}) \quad (1)$$

$$\%\ \text{sodium} = 100 \times \left[1 - \frac{\text{hardness}}{0.404\,K_d + 0.246\,(\text{alkalinity})}\right] \quad (2)$$

where K_d is the diluted conductance in micromhos and both alkalinity and hardness are in parts per million as $CaCO_3$.

The method is of value in evaluating waters for agricultural use.

Table I illustrates the results obtained from several waters differing greatly in composition. Nos. 1 and 5 are synthetic waters taken from the examples of Gustafson and Behrman (*1*), 4 and 9 are taken from their table of natural waters; the others are natural waters tested in this laboratory. These waters represent extremes; the best results are obtained on moderately mineralized waters having no one constituent greatly in excess of others having the same valence sign.

The method will fail in the presence of high potassium or ammonium concentrations. It is not applicable outside the pH range of 6 to 9.

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RECEIVED February 9, 1948.

Determination of Wax Content of Raw Cotton Fiber

Nonvalidity of Preliminary Treatment with Hydrochloric Acid

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THE accuracy with which the known constituents of raw cotton fiber may be determined is of importance in work directed toward the detection and identification of unknown constituents. Knecht and Streat (*3*) and Fargher and Higginbotham (*2*) have cast doubt upon the accuracy of wax values obtained by the usual methods. They showed that higher wax values could be obtained by disrupting the fiber structure with hydrochloric acid prior to extraction of the wax, but did not offer evidence that the additional extracted material was wax.

With the advent of the Conrad alcohol extraction method (*1*), which provides for a phasic separation of the wax from other substances, it seemed likely that an answer to this question could be found. However, even with this method, higher values were obtained with raw cotton following treatment with hydrochloric acid. A sample of kier-boiled cotton fabric showed no increase in wax value following treatment with hydrochloric acid, indicating that the substance or substances responsible for the higher values were removed by kier boiling. When raw cotton fiber was given a preliminary exhaustive extraction with water it showed little or no increase in wax value due to treatment with hydrochloric acid.

Data on six different samples of raw cotton fiber are given in Table I. Each value is the average of four determinations with a standard deviation of about 0.04%. The treatments prior to extraction with alcohol according to the Conrad method were: (1) extracted without preliminary treatment; (2) ground to pass a 60-mesh screen in a Wiley mill; (3) fumed with hydrochloric acid by being placed in a desiccator over concentrated hydrochloric acid for 24 hours; (4) wetted with hot water and extracted with water in a Soxhlet extractor for 48 hours, dried in vacuum oven at 60° C., and air equilibrated; (5) water-extracted as described, dried, air equilibrated, and placed in a desiccator over hydrochloric acid for 24 hours. The data show that the sub-

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Table I. Wax Values Obtained with Conrad Method on Raw Cotton Fiber Subjected to Preliminary Treatments

Variety or Kind of Cotton	Preliminary Treatment Prior to Alcohol Extraction				
	None, % M.F.B.[a]	Ground, % M.F.B.	Fumed with HCl, % M.F.B.	Water extracted, % M.F.B.	Water extracted and fumed with HCl, % M.F.B.
Empire	0.72	0.79	0.90	0.73	0.81
Unknown	0.55	0.62	0.82	0.58	0.60
Immature	1.14	1.38	1.54	1.08	1.24
Stoneville 2B	0.69	0.77	0.98	0.80	0.91
Empire	0.90	0.86	1.21	0.80	0.78
Wilds	1.04	0.94	1.55	0.93	1.03
Av.	0.84	0.89	1.17	0.82	0.90

[a] Moisture-free basis.

stance or substances responsible for the increased wax values following treatment with hydrochloric acid are water-soluble. Hydrochloric acid converts these substances into a material that behaves like wax in the Conrad method and presumably in other wax methods. The nature of these water-soluble substances is unknown. Their behavior is similar to that exhibited by fructose when introduced into purified cotton linters; but the sugar content of raw cotton fiber is not large enough to explain all the increase produced by hydrochloric acid treatments.

Cotton fibers should not be treated with hydrochloric acid prior to extraction of wax. Without such treatment values nearer to the true wax content are obtained.

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(2) Fargher, R. G., and Higginbotham, L., *Textile Inst. J.*, **18**, 283–7 (1927).

(3) Knecht, E., and Streat, G. H., *J. Soc. Dyers Colourists*, **39**, 73–7 (1923).

Received May 27, 1948.

CRYSTALLOGRAPHIC DATA

Contributed by Armour Research Foundation of Illinois Institute of Technology

14. Pimelic Acid

PIMELIC acid (heptanedioic acid) can be crystallized from water (*2*), ethyl acetate (*1*), and the melt (*3*). The crystals from water are suitable for microscopic examination as well as single crystal x-ray diffraction studies.

Pimelic acid is reported (*3*) to exist in two polymorphic forms with a transition temperature of 74.75° C. This fact may explain some of the divergence in the reported data (*1, 2, 3*). There is, however, no confirmation of the existence of polymorphs in the present work.

Crystal Morphology (determined by W. C. McCrone).

Crystal System. Monoclinic.

Form and Habit. Plates and tablets lying on 001 with the forms: basal pinacoid {001}; orthopinacoid {100}; and prisms {120}.

Axial Ratio. $a:b:c = 4.551:1:2.043$; $3.691:1:2.058$ (*2*).

Interfacial Angles (Polar). $120 \wedge \bar{1}20 = 46°$; $100 \wedge 001 = 49°$.

Beta Angle. 131°; 130° 41′ (*1*); 137° 14′ (*3*); 105° 40′ (*2*).

X-Ray Diffraction Data (determined by J. Whitney and I. Corvin).

Space Group. $C_{2h}^{5}(P_{1}^{2}/c)$ (*1*); C_{2h}^{6} (*3*).

Cell Dimensions. $a = 22.12$ Å.; $b = 4.86$ Å.; $c = 9.93$ Å.; $a = 9.93$ Å.; $b = 4.82$ Å.; $c = 22.12$ Å. (*1*); $a = 22.20$ Å.; $b = 9.59$ Å.; $c = 45.4$ Å. (*3*).

Formula Weights per Cell. 4; 32(*3*).

Formula Weight. 160.17.

Density. 1.323, buoyancy (1.34, x-ray).

Principal Lines

d	I/I_1	d	I/I_1
8.56	0.58	2.36	0.33
7.64	0.05	2.29	0.11
4.81	0.09	2.22	0.23
4.59	0.86	2.17	0.15
4.28	Very weak	2.12	0.05
4.03	0.52	2.08	0.02
3.87	0.20	2.01	0.08
3.74	1.00	1.93	0.03
3.44	0.08	1.85	0.10
3.33	0.17	1.81	0.09
3.20	0.98	1.76	Very weak
3.05	0.03	1.72	0.03
2.92	0.02	1.69	0.02
2.82	0.10	1.65	Very weak
2.78	0.10	1.63	Very weak
2.67 2.60	0.02	1.62	Very weak
2.52	0.08	1.59	0.09
2.46	0.05		

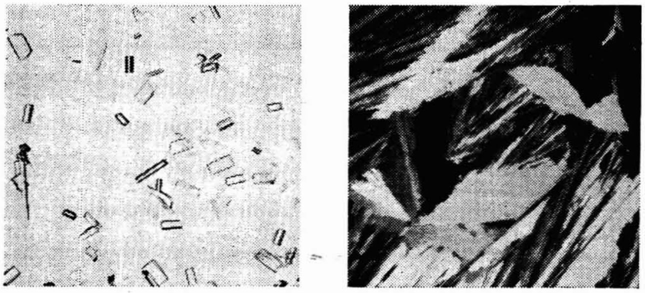

Figure 1. Pimelic Acid

Left. **Crystals from water on a microscope slide**
Right. **Fusion preparation**

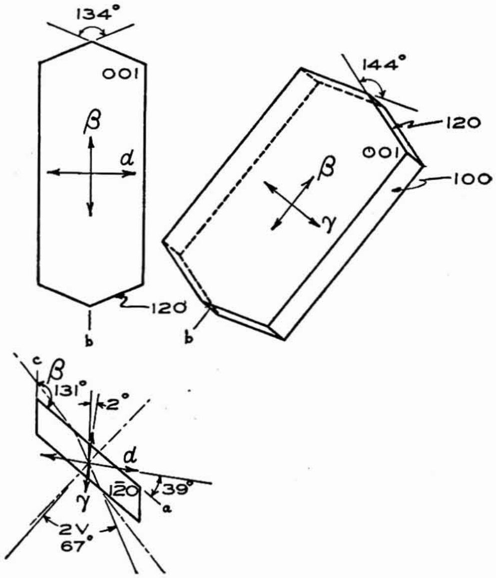

Figure 2. Orthographic Projection of Typical Crystal of Pimelic Acid

Optical Properties (determined by W. C. McCrone).

Refractive Indices (5893 Å.; 25° C.). $\alpha = 1.482 \pm 0.001$. $\beta = 1.508 \pm 0.002$. $\gamma = 1.580 \pm 0.001$.

Optic Axial Angles (5893 Å.; 25° C.). $2V = 67° \pm 2°$.

Dispersion. Very slightly inclined dispersion, $v > r$.

Optic Axial Plane. 010.

Sign of Double Refraction. Positive.

Acute Bisectrix. $\gamma \Lambda c = 2°$ in obtuse β.
Extinction. $\alpha \Lambda a = 39°$ in obtuse β.

Molecular Refraction (R). $\sqrt[3]{\alpha\beta\gamma} = 1.523$. R(calcd.) = 37.6. R(obsd.) = 37.0.

THERMAL DATA (determined by W. C. McCrone).

Pimelic acid melts at 103° to 105° C. and resolidifies spontaneously to give long rods elongated parallel to b. The optic axial plane lies crosswise of these rods and the crystals may show Bx_a, Bx_o, or optic axis interference figures; the Bx_o or optic axis figures are most common. The optic axial angles are $2H_\alpha = 110°$; $2V_\alpha = 111°$; $2V_\gamma = 67°$.

In a mixed fusion with thymol the crystals are not too well formed but usually show square ends with beta parallel to the length less than the refractive index of thymol; the other index is usually gamma or gamma prime and therefore *greater than* thymol.

Pimelic acid shows boundary migration at temperatures just below the melting point. This is evident from the penetration of one crystal into its neighbor after primary crystallization is complete.

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(1) Caspari, *J. Chem. Soc. London*, **1928**, 3235.
(2) Groth, "Chemische Kristallographie," Vol. 3, p. 495, Leipzig, Engelmann, 1910.
(3) Latour, *Compt. rend.*, **201**, 479 (1935).

SCIENTIFIC COMMUNICATIONS

Thioacetamide in Place of Gaseous Hydrogen Sulfide for Precipitation of Insoluble Sulfides

THIOACETAMIDE has been successfully used in place of gaseous hydrogen sulfide in the development of new methods for qualitative analysis of cations of Groups II and III.

Thioacetamide does away almost entirely with the disagreeable odor associated with gaseous hydrogen sulfide. A water solution is added directly to the solution from which the cations are to be precipitated.

Thioacetamide eliminates the use of hydrogen sulfide cylinders, generators, and other undesirable means of obtaining gaseous hydrogen sulfide.

No great excess of thioacetamide is necessary. Nearly equivalent amounts of the organic sulfide and the cations will bring about complete precipitation of the insoluble metal sulfides.

The hydrolysis of thioacetamide gives a relatively low concentration of the sulfide ion in solution, which favors the rapid coagulation and filtration of the insoluble sulfides.

The time required for the complete precipitation of the insoluble sulfides by the use of thioacetamide is less than the overall time required when gaseous hydrogen sulfide is used.

Thioacetamide is an easily obtainable commercial product. The odor is not unpleasant. It is soluble in water, keeps well in solution, and per unit precipitation is less in cost than gaseous hydrogen sulfide.

H. H. BARBER
EDWARD GRZESKOWIAK

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Automatic Paper Chromatography

PAPER chromatography is being revived as an important adjunct in the analysis and identification of protein hydrolyzates, antibiotics, and otherwise difficultly separable mixtures. We are engaged in the development of instruments to record continuously the process of diffusion through special paper matrices which not only reveal the dynamics of the process but yield quantitative analyses of the mixtures. Optical, conductometric, and dielectric criteria of diffusion have been found useful in this technique and possess individual advantages in specific applications.

We have succeeded in recording the chromatographic separation of microgram quantities of dye mixtures on paper by an optical method. We have prepared restricted rectangular channels on ordinary filter paper by embossing the paper with paraffin barriers, similar to the familiar techniques of confined spot tests. A tiny spot of the dye mixture is deposited in the channel. Somewhat beyond the sample, a fine spot of monochromatic light is focused on the paper, and on the opposite side of the sample a suitable eluting solvent is added from a microcapillary. As the eluting liquid passes over the sample, the components of the mixture are driven preferentially toward the light scanning zone. As each of these passes the spot of light, the transmittancy and reflectivity of the paper are modified. We have followed the process by focusing the emergent light on a photomultiplier tube and measuring the photocurrent with a Brown Electronik recording potentiometer. Complete separation of binary mixtures in microgram amounts has been achieved in 45 seconds. The speed and sensitivity are largely due to the use of the confined channel.

The details of this as well as the nonoptical methods are being submitted to ANALYTICAL CHEMISTRY.

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Book Review

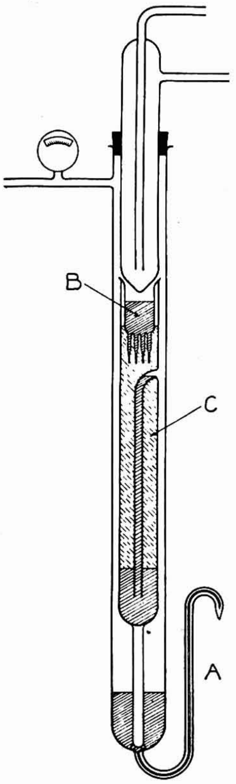
Symposium on Spectroscopic Light Sources. Special Technical Publication 76. 80 pages. American Society for Testing Materials; 1916 Race St., Philadelphia, Pa., 1948. Price, $2.

The paper and discussions appearing in this volume were presented at the 1946 annual meeting of the American Society for Testing Materials, held in Buffalo, N. Y., under the sponsorship of Committee E-2 on Spectrographic Analysis. In addition to the introduction by E. B. Ashcraft, Monsanto Chemical Co., it includes the following papers: "Present Status of Excitation in Spectrographic Analysis," B. F. Scribner, National Bureau of Standards; "Controlled Spectrographic Spark Source," J. H. Enns and R. A. Wolfe, University of Michigan; "Some Properties of Gas Discharges Used as Spectral Sources," R. C. Mason, Westinghouse Research Laboratories; and "Short-Period Phenomena in Light Sources," by G. H. Dieke, Johns Hopkins University. The prepared discussions were presented by R. H. Bell, Lucius Pitkin, Inc.; Wendell R. Koch, U. S. Army Air Corps; C. J. Neuhaus, International Nickel Co.; E. K. Jaycox, Bell Telephone Laboratories; J. R. Churchill, Aluminum Company of America; M. F. Hasler, Applied Research Laboratories; J. L. Saunderson, Dow Chemical Co.; P. R. Irish, Bethlehem Steel Co.; and L. W. Strock, Saratoga Springs Foundation.

CORRESPONDENCE

Small-Scale Continuous Liquid-Liquid Extraction at Superatmospheric Pressures

SIR: Continuous extraction of 1 to 25 ml. of aqueous solutions in order to remove organic chemical solutes has sometimes proved to be a useful analytical tool (*1*). The method fails when the partition coefficient is distinctly unfavorable. The apparatus described here improves such an unfavorable partition coefficient by operation at pressures of 16- to 17-pound gage or higher. The increased boiling point of the liquids in the system under these conditions permits operation in what may be a more favorable temperature range. Furthermore, volatile gases (such as ammonia) which tend to decrease ionization of organic amines can be retained in this apparatus and thus also may improve the partition coefficient.



The apparatus illustrated serves to extract 40 to 45 ml. of aqueous solution when the outside containing tube is 30 mm. in inside diameter by 350 mm. long. The aqueous solution is retained over a layer of chloroform in tube *C*, which is 25 mm. in inside diameter by 195 mm. long. It is equipped with a tube 4 mm. in inside diameter, which is insealed 50 to 100 mm. from the top (depending on the density of the aqueous solution to be extracted) and reaches as close to the bottom as possible. Inserted loosely into this aqueous solution reservoir is a cup 20 mm. in inside diameter by 35 mm. long, to which are sealed seven small tips which terminate in openings 0.5 mm. in inside diameter. A larger number of tips is disadvantageous, as the chloroform which drips through them tends to accumulate unless the spacing is adequate. This is especially true when the density of the aqueous solution is near that of chloroform.

The aqueous solution holder, *C*, is supported out of the boiling chloroform reservoir at the bottom of the outside container by a glass rod 8 mm. in outside diameter, which is trifurcated at its bottom to permit free passage of chloroform through the capillary tube, *A*. Three indentations (not shown) in the outside container may be used to center *C*, but they are usually not necessary if the cold finger condenser at the top of the apparatus is inserted so that its tip extends into the cup. As the indentations may tend to weaken the pressure resistance of the outside container, they may well be avoided.

The cold finger is retained by a rubber stopper which is securely wired against pressure around the flange at the top of the outside container. Below this flange is sealed an 8- to 10-mm. side arm to which are attached the pressure source and a suitable gage.

During operation the lower end of the apparatus is inserted into a heating bath in order to boil the chloroform up past tube *C*, which it heats, and then up to the condensing surface, from which it drips through the aqueous solution and thence out of the insealed tube back into the pool of chloroform at the bottom of the apparatus. After extraction is considered to be complete the apparatus is cooled and the pressure released. The tip of *A* is then broken (the illustration shows this tip after it has been shortened by much use) and the extract is forced over and out of the apparatus. If completeness of extraction is to be tested, a fresh lot of chloroform may then be sucked in, after which the tip is sealed and the extraction continued.

The size of this apparatus has been reduced by half in order to utilize smaller volumes and higher working pressures of air or ammonia. The drip cup on the smaller apparatus has only four tips symmetrically placed. In either case the drip cup and tube *C* should be equipped with small holes at the top, so that they can be removed from the apparatus by a wire hook.

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(1) Wayman, M., and Wright, G. F., IND. ENG. CHEM., ANAL. ED., **17**, 55-6 (1945).

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The Analyst's Calendar

Subgroup of North Jersey Section

The third meeting of the Analytical Subgroup of the North Jersey Section, AMERICAN CHEMICAL SOCIETY, will be held February 9 at 8 P.M. at the cafeteria of Eimer & Amend, Greenwich & Morton Sts., New York, N. Y. The speaker will be Harvey Diehl, Iowa State College, who will discuss organic compounds as analytical reagents.

Prior to the meeting there will be an inspection tour of the Eimer & Amend plant at 5 P.M., followed by dinner in the cafeteria at 6:15 P.M. Those wishing to attend the dinner as guests of Eimer & Amend should make reservations with Al Steyermark, Hoffmann-LaRoche, Inc., Nutley, N. J., not later than February 1.

Fourth Annual Analytical Symposium. Hotel William Penn, Pittsburgh, Pa., January 20 and 21, 1949.

Metropolitan Microchemical Society of New York. American Museum of Natural History, New York, N. Y., February 25 and 26, 1949.

Second Symposium on Analytical Chemistry. Louisiana State University, Baton Rouge, La., March 2 to 5, 1949.

Second Annual Summer Symposium on Analytical Chemistry. Wesleyan University, Middletown, Conn., June 24 and 25, 1949.

Fourth Instrument Conference and Exhibit. Municipal Auditorium, St. Louis, Mo., September 12 to 16, 1949.

AIDS FOR THE ANALYST . . . . .

Pump for Volatile or Toxic Liquids in Viscometers.

John W. McElwain, National Bureau of Standards, Washington, D. C.

In using a viscometer of the Ostwald type it is necessary to apply either suction or pressure to transfer the test liquid to the upper reservoir before making a measurement. Ordinarily this suction or pressure is applied by mouth. When toxic or irritating liquids like benzene, cresol, or formic acid are used, an external source of suction or pressure is practically mandatory. In addition, in precise work, especially with concentration-sensitive systems such as solutions of high polymers in liquids of high volatility, it is essential to avoid a change of concentration by loss of solvent vapor. This requires either a closed system or a means for presaturating air introduced into the viscometer. Several designs have been mentioned in the literature for prevention of solvent loss either during the loading operation or during a run (Barr, G., "A Monograph of Viscometry," p. 222, London, Oxford University Press, 1931; Hatschek, E., "Viscosity of Liquids," pp. 45, 52, New York, D. Van Nostrand Co., 1928). All require auxiliary pumps, or must be made by an expert glass blower.

In the course of the measurement in this laboratory of viscosities of dilute solutions of high polymers in toxic and volatile solvents, the arrangements illustrated in Figure 1, (*a*) and (*b*), were found convenient. These can be adapted to standard equipment in any laboratory.

A rubber pump bulb, *P* [Figure 1(*a*)], with valves at V_1 and V_2 permitting air flow in the indicated direction, operates (when stopcock at *A* is closed) to push the test liquid into the upper reservoir, *R*, to a level above the mark, M_1. Opening the stopcock permits a measurement of flow time in the usual manner. It is necessary that the pump bulb be correctly oriented vertically to ensure operation of the valves and that the apertures of the stopcock and connecting tubes be sufficiently large to allow passage of air through the system without appreciable viscous resistance.

The arrangement for use with an Ubbelohde viscometer is shown in Figure 1(*b*). The three-way stopcock is set at position *A* when the liquid is to be transferred to the upper reservoir, *R*. Setting the stopcock as in *B* permits operation in the usual manner.

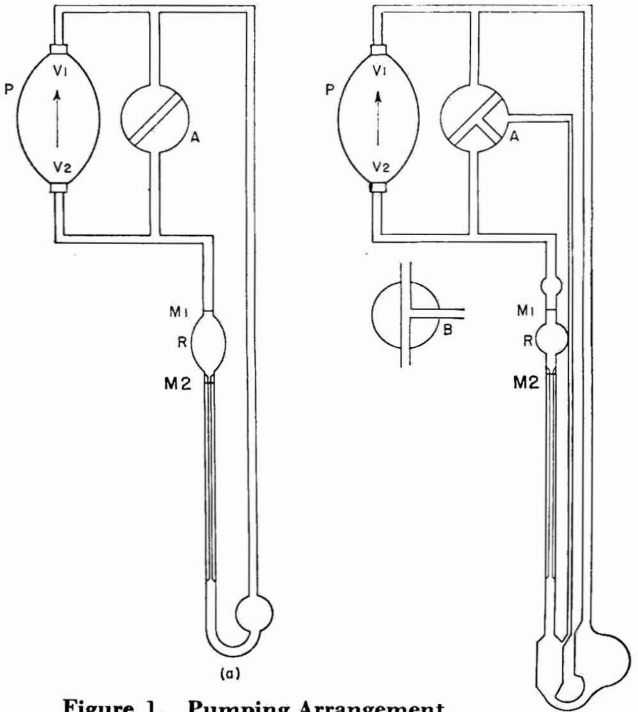

Figure 1. Pumping Arrangement for Viscometers

Stopcock Grease for Organic Vapors.

Paul T. Davis, Jerome Grossman, and B. L. Harris, Johns Hopkins University, Baltimore 18, Md.

In the course of adsorption studies of organic vapors by solid adsorbents it was necessary to use a stopcock lubricant that would not absorb organic vapors, would allow a vacuum of the order of 10^{-4} mm. of mercury or better to be obtained, and would be stable for several days, eliminating the need for frequent regreasing.

After a study of available materials, samples and literature on completely fluorinated lube oil fractions were obtained from the Jackson Laboratory of E. I. du Pont de Nemours and Company, Inc. The materials were prepared by the method of Fowler *et al.* [*Ind. Eng. Chem.*, **39**, 292–8 (1947)] and are listed as insoluble in chloroform, carbon tetrachloride, methanol, ethyl acetate, acetone, petroleum ether, ethyl ether, benzene, and dichlorobenzene. Two cuts, Nos. 5 and 7, were received for study. The boiling ranges were, respectively, 170° to 190° and 210° to 240° C. at 10 mm. of mercury. A mixture of one part of each cut has been used in an apparatus handling butadiene vapor in which the stopcocks have not been regreased for 6 months and no apparent effects have been observed. A mixture of 5 parts of cut 7 to 1 part of 5 has been used in an apparatus handling benzene vapor; no variation of pressure (measured to ±0.1 mm. of mercury) was observed when samples of benzene were allowed to stand isolated in the system in contact with three stopcocks and one ground joint for 24 hours at constant temperature (25° C.). The former mixture is of such viscosity that a stopcock lubricated with it can be easily but slowly turned at room temperature. The latter mixture required slight heating to turn the stopcocks easily.

It is probable that cut 6, boiling range 190° to 210° C. at 10 mm., would prove useful for this purpose without blending. This was not tested, because the above mixtures solved problems satisfactorily. This grease can be used not only for organic vapors but probably for polar vapors as well and hence one grease can be used for all applications in vacuum technology.

Two other materials were tested and found unsatisfactory. The first was a sample of Glydag, a dispersion of colloidal graphite in glycerol supplied by the Acheson Colloids Corporation. This previously had been found effective for 2 to 3 days if prepared by thoroughly pumping off absorbed water (Harris, B. L., dissertation, Johns Hopkins University, 1941). Lubricant prepared by this technique was stable for not more than one day, owing to the absorption of atmospheric moisture; this was possibly due to the use of a different sample of material than that previously tested.

Two batches of a lubricant, made as suggested by Pearlson [Ind. Eng. Chem., Anal. Ed., **16**, 415 (1944)] from cellulose acetate in tetraethylene glycol, were prepared using different cooking schedules. Neither was apparently affected by organic solvents when a small smear was immersed in the solvent, but both absorbed benzene from the vapor phase; the pressure of a sample of benzene vapor fell steadily when confined in the isolated tested vacuum system.

The authors wish to thank the Jackson Laboratory of E. I. du Pont de Nemours and Company, Inc., for making the samples available for this study.