Increasing the Services of the Division of Analytical and Micro Chemistry

W. A. KIRKLIN, chairman of the Division of Analytical and Micro Chemistry, speaking before the Fourth Pittsburgh Analytical Symposium, raised the question of what can be done within the division to meet the growing needs of specialized fields, yet fields that are an integral part of modern chemical analysis.

In recent years the division has sponsored a number of symposia at national meetings, supplementing the regular program of papers. At the St. Louis session of the 114th meeting, two such symposia were held: one on current developments in the application of chemical microscopy, the other on new electrical methods of analysis; at the 113th meeting the design of experiments for developing new analytical methods was thoroughly discussed; at the 112th meeting a full-day session was devoted to the purity and identity of organic compounds; and the 111th meeting was featured by a symposium on statistical methods.

We believe the idea of specialized symposia should be encouraged and expanded at national meetings of the Society. The introduction of the idea of summer symposia, cosponsored by the division and ANALYTICAL CHEMISTRY, offers further opportunity for exhaustive treatment of special subjects. The possibility of direct assistance from local sections and other groups is evidenced by the annual symposia of the Analytical Division of the Pittsburgh Section, the Symposium on Modern Methods of Analysis, conducted in March 1948 by the Minnesota Section, and the one-day Symposium on Instrumental Methods of Chemical Analysis, held by the New York Section on November 20.

Indeed, we are delighted to see the increasing interest in analytical chemistry at the local section level as indicated, among other things, by the sponsorship of a series of eight lectures on polarography, spectroscopy, x-ray and electron diffraction, electrophoresis, and ion exchange, sponsored by the Eastern New York Section last winter. Other sections likewise are sponsoring lectures and courses of direct interest to analysts.

Most promising of all is the rapid growth in the number of local sections that have established analytical groups within the local section framework. Here is, perhaps, the finest opportunity of all to bring analysts together interested in highly specialized fields, with the full blessing and support of the Society.

Dr. Kirklin and the Executive Committee of the division are seeking ideas from analysts for expanding the division's service.

We would like to make one suggestion to start the ball rolling. Is it not feasible at national meetings to arrange half-day round-table discussions on such subjects as polarography, infrared spectroscopy, etc., with the discussion mechanically recorded and later digested by each chairman, for publication in ANALYTICAL CHEMISTRY in two- or three-page reports? The round-table discussion could be scheduled after the more informal divisional program has been completed and when there would be no disturbing conflicts. Much of its success would depend upon the proper selection of discussion leaders. Events of the past few years certainly have demonstrated that we do not lack leadership among analysts.

The round-table form of meeting is gaining in popularity among scientists in many fields. It has a very useful function, quite different from the presentation of formal papers. One of the chief criticisms leveled at our general meetings is the lack of time for informal discussion of the papers presented. We see very little possibility of providing such time in view of the ever-increasing number of excellent papers presented at our national meetings. Round-table discussions seem to us to offer possibilities for more active participation by the analysts who attend, the opportunity to exchange ideas and experiences of great practical value which are not widely shared simply because no means are provided.

We are suggesting essentially an extension of the corridor groups which are present at every meeting. The forum idea would expand the opportunities for the dissemination of information, not only among those attending the meeting but among the stay-at-homes, through publication of a well-edited digest that could be read by 30,000 analysts here and abroad.

Perhaps a start of modest proportions could be made at the fall meeting in Atlantic City, if the proposal is viewed favorably. Two or three subjects could be selected for the initial attempt. With a very large segment of analytical chemists within easy travel distance of Atlantic City, the likelihood of success would be increased.

First Annual Review of Analytical Chemistry[1]

THE first part of this First Annual Review of Analytical Chemistry was published in the January issue. It consisted of 29 articles covering the developments in fundamental analysis. The second part of the review, devoted to the practical applications of analytical developments in various industrial fields, consists of 11 articles and occupies the following 89 pages.

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COATINGS

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THE analysis of coatings is a broad topic and for this brief, critical review of the literature, it is practically necessary to define and limit the field of view. The term "coatings" might embrace every material that could be spread on a surface or incorporated into a film. By far the most common matrices, however, are those organic high-polymeric substances into which may be incorporated oils, plasticizers, waxes, fillers, pigments, etc. For brevity, the authors have arbitrarily omitted important classes of coating materials such as vitreous enamels and metallic platings.

The term "coating" implies that the material has been applied. Applied coatings may be divided into those whose deposition on the substrate is accompanied by an insolubilizing chemical change, and those that are deposited without chemical change. From the analytical point of view, the former type presents the greater difficulties, because the insoluble nature of the coating seriously restricts the application of general chemical analytical methods. In such instances, physical properties offer the first line of investigation, with the possibility of supplementing these data with those obtained by vigorous attack and chemical analyses of the resulting products. On the other hand, the latter (lacquer) type, which is deposited without chemical change, may also be removed without chemical change by the use of physical solvents. For such materials the scheme of analysis becomes essentially the same as that for the unapplied (original) material. Both insoluble and soluble types of organic coatings are considered in this review of the literature.

An analyst encountering a new type of material probably will search first for a ready-made general scheme. Failing to find a whole plan he will look for specific determinations which appear to be applicable. Still without success, he will search for published data on determinative chemical and physical properties and methods of obtaining them. Therefore, relevant literature published in the last few years and not included in the general schemes reviewed is classified here according to these three categories.

As starting points, the authors use the dates of publication of the five volumes of "Protective and Decorative Coatings," edited and inspired by the late J. J. Mattiello, and published from 1941 (Vol. I) to 1946 (Vol. V) (*50–54*). This monumental work embodies 3301 pages of text and was the work of 125 different authors, who donated their time for the establishment of a research scholarship fund at Polytechnic Institute of Brooklyn. These books were intended primarily for technical people who are engaged in the manufacture, formulation, or consumption of coating materials. There is, however, a wealth of material that may be classified in the three categories given above. Unfortunately, in the indexes of the first four volumes, the term "analysis" is scarcely to be found. Volume V, written expressly for analysts and indexed by an analyst, is most important and is reviewed first.

HIGH POLYMERIC MATERIALS

General Analytical Schemes. A very general scheme of resin analysis which can be applied to both soluble and insoluble organic coatings is proposed by Stafford and Williams (*54*).

They begin by searching for a physical solvent that will reduce the coating to a "solution" which can be analyzed like an unapplied material, but with consideration of possible chemical changes. Failure in complete removal by a solvent is followed by mechanical removal with subsequent destructive distillation, but details of this procedure are not given. Next, the scheme is to determine solubility behavior (with possible resin-from-resin separation), physicochemical properties, behavior on ignition, chemical elements, color reactions, and determinative derivatives. A "master table" is included for the most significant of these properties among major classes of resins, elastomers, and waxes. Directions for thirteen color-reaction tests are given to establish a broad classification, but these are not used in any relevant sequence. The physicochemical properties to be determined are: refractive index, specific gravity, softening point, acid and saponification values, and iodine value. Directions for measuring these properties are given, together with tables which are determinative for many individual resins. There also are brief discussions of the following special methods: x-ray diffraction and radiography, spectrophotometry in the ultraviolet, visible, and infrared regions, and Raman spectroscopy. Finally, there are four examples of actual use of the scheme: an applied "hot-melt" coating; an unapplied water-emulsion paint; a molding resin; and a molded resin. In the text there are 215 references to the literature, together with 42 "supplemental" (later) references. Stafford and Williams explain that their scheme is incomplete and serves mostly as a set of suggested plans of attack. The work, extensive as it is (164 pages) is relatively weak on applied coatings. It was not within the scope of the chapter to include plasticizers, fillers, or pigments.

There are relatively few general discussions of the analysis of applied materials only. One of these is based on physical methods, especially microscopical ones, and is called "resinography" by the authors, Rochow and Gilbert (*54*). By these means one may begin with very general information about a surface of a coating such as homogeneity, grain, design, cracks, or voids. More important, resinography gives much information about the internal structure of individual layers, such as the

number, thickness, uniformity, and homogeneity. The method also gives information about cracks, voids, separate resinous phases, and kinds of fillers.

This information is obtained by use of various types of microscopes and much (too much) space is devoted to the description (without evaluation) of the mechanics, optics, and various techniques involved. Some space is given, however, to the determination of microhardness, chemical spot tests, spectrochemical analysis, microscopical qualitative chemical analysis, physical quantitative analysis, specific gravity, and refractive indexes. Altogether, there are 76 references.

Like metallography and mineralography, resinography serves to distinguish among physical-chemical phases and to depict their mode of association. Thus, if two resinous ingredients are highly incompatible, like a phenolic resin plus GR-S or reclaimed rubber in virgin rubber, light microscopy will serve to reveal and identify them (among such limited possibilities). In resins which are light-microscopically homogeneous, the electron microscope is beginning to show structure which may become determinative as well as descriptive. In its present state, however, resinography serves chiefly to identify fillers according to their biological mineralogical, or physical-chemical species.

The principal criticism of this dissertation is that it does not give to the great varieties of "surface" coatings space commensurate with their importance. Only slightly more information is given in two subsequent papers (84, 85). The answer is that further resinographic information is still unknown.

A very recent paper by Lysaght (43) on the practice and interpretation of hardness tests on plastics serves chiefly to introduce the Knoop indenter which makes an elongated-rhomb impression whose long diagonal is affected relatively little by elastic recovery. The Knoop indenter when used on the Tukon tester becomes a microtester of the hardness of individual microscopic constituents of a coating.

In the 1948 "Modern Plastics Encyclopedia" (56–70) there is a chapter on "Identification of Plastics" (56) which is coordinated with the "Plastics Identification Chart" (59). Although the broad subject of plastics is covered, much of the information is directly applicable to organic coatings.

Many procedures for decomposition by heat are considered, besides that which is specified for the results on 38 types and varieties of plastics given in Table I of the plastics identification chart. The behavior of 18 thermoplastics in 16 organic solvents is given in Table II, while the text specifies special solvents for 9 of the resin types that are insoluble in the 16 solvents listed in the table. Seventeen color tests indicating many of the resins used in coatings are given in Table III. The text complements the table by repeatedly referring to the literature for specific chemical tests such as those applicable on the products of pyrolysis; reaction of elastomers in mixed sulfuric and nitric acids and in various mixtures of benzene, petroleum ether, and aniline; qualitative and quantitative elemental chemical analysis; depolymerization in alkali, in acid, or by dry distillation and subsequent identification of the products; and many others. Eight "successful" microscopical staining tests given in Table IV are particularly adaptable to the resinographic study of the surfaces and cross sections of coatings.

Many methods are mentioned for the separation of mixtures of plastic materials, particularly those used in coatings. In the text there is a table of "approximate densities" for 25 resins and a table of characteristic fluorescence colors in ultraviolet light for 31 resins. Other physical-chemical properties are mentioned, such as x-ray diffraction, infrared absorption, hardness, and dielectric constant. Sixty-four references are cited. This comprehensive bibliography, the collection of determinative data, and the critical aspect of the text make the chapter of foremost value to the analyst of coatings. Good as it is, however, the present authors can still wish that it were more extensive commensurate with the encyclopedic title of the work.

The text mentioned above is complemented by the 1948 series of 12 charts.

In the plasticizers chart (67) at least several determinative properties are listed for plasticizers. Similar properties are listed for solvents in the corresponding chart (69). The adhesives chart (60) serves the analyst chiefly by listing trade names and manufacturers corresponding to chemical terms, solvent action, advantages and disadvantages, and effectiveness as a bond with typical materials. The coatings chart (62) serves in very much

the same manner and should be consulted before experimental analysis is begun. Eleven types of synthetic rubbers are listed in the corresponding chart (70) together with their manufacturers, and 19 test properties. While the low pressure laminating resins chart (65) lists products of 13 manufacturers, and is larger, it does not list much determinative information. The laminates properties chart (64) is entirely new and contains much the same information as the general plastics properties chart and could be useful in identifying thermoreacted, high-pressured coatings. The plastic films chart (66) is also new and contains some information that may be useful concerning 17 plastics which might be encountered as coatings.

Crossley's discussion (23) of the various aspects of paint analysis includes a section on the examination of competitive products. The pigment is centrifuged from the vehicle and tested in the usual qualitative inorganic manner. Some possible spot tests on the pigment are indicated. Special mention is made of the simultaneous determination of maleic and phthalic acids, the identification of phenolic resins, and the determination of the oil content of distempers.

An article by Gordijenko and Schenk on the qualitative organic analysis of complex organic compounds on the basis of their precipitability has recently been abstracted (34). "Tests with 250 compounds, representing a great variety of resins, elastomers, plasticizers, waxes, oils, and adhesives demonstrate that complex organic compounds can conveniently be identified on the basis of their behavior in a series of solvents and solvent mixtures of varying polarity." Precipitation behavior in twelve solvents is tabulated; products are identified by German trade names. The system appears to be particularly suited for the identification of resins.

Analytical schemes, with interesting titles but with little else available to the present reviewers, include: Brennan on the analysis of resin finishes (15); Medina-Castellanos on the chemical analysis of plastics (55); Nijveld on the individual characteristics of plastics including a tabulation of the results of comparative qualitative reactions (74); Oschmann on the application of classical analytical methods to identification of certain synthetic resins (75); and Zeidler on the chemical inspection of paints and lacquers, including a general review of their chemical analysis (108).

Although it contains no empirical data, Mark's theoretical discussion (48) of the mechanical properties of high polymers in general should be included in this review. Under the headings "Use of new chemical systems in preparing high polymers" with five subheads, and "Details of chain structure and mechanical properties of polymers" with three subheads, the theoretical aspects are ably and thoroughly covered.

Chatfield's (21) comprehensive book on varnish constituents includes chapters on varnish, oils, acids, monoglycerides, natural oil varnish resins, natural spirit varnish resins, modified natural resins, synthetic resins, solvents and diluents, plasticizers, driers and other metallic soaps, antioxidants, pitches, waxes, and rubbers. Analytical information is scattered among the various categories.

In his book on coating and ink resins, Krumbhaar (41) devotes a chapter to the chemical characteristics of resins. Directions for individual determinations, both physical and chemical, are included, but no attempt is made to arrange the tests in an analytical scheme for individual resins. The author states: "Elaborate analytical schemes and systematic procedures have been worked out for the identification of individual resins within the whole range of synthetic resins. Applying the suggested analytical procedures to the coating and ink resins under discussion, vague and inconclusive results are obtained which in no way warrant the considerable time and effort involved in such analyses."

A number of other books (6, 20, 24, 47, 99, 106) dealing with high polymeric materials have recently appeared. Although they are sources of fundamental information for the analyst neither

"analysis" nor "identification" appears in the index of any of these.

The Bradley survey for the A.S.T.M. (14) is limited to the critical evaluation of existing methods employed in the testing of common types of resins sold in solution and solid form, and includes recommendations for further investigation. As a result of the Bradley survey, Subcommittee XI of Committee D-1, A.S.T.M., was organized in 1946 under the chairmanship of the late J. J. Mattiello. The subcommittee, now under the chairmanship of C. F. Pickett of Aberdeen Proving Ground, is actively engaged in the investigation of resin analysis, with ten working groups evenly divided between methods and materials. This program will result in A.S.T.M. specifications with respect to the methods; it is anticipated that the materials investigation will lead to a flexible general scheme of resin analysis.

Skinkle (92), in suggesting a general scheme for the analysis of textile additives, first isolates the finishing agents by successive extraction with selective solvents. The probable constituents of each solvent fraction are itemized. Each extract is then tested further with a series of accepted qualitative tests. Although the procedure is well organized, its scope is so ambitious that unavoidable interferences and discrepancies are possible. The A.A.T.C.C. Subcommittee on Standard Methods of Determining Textile Finishes, under the chairmanship of J. Edward Lynn of the American Cyanamid Company, conducted an inter-laboratory test of the procedure and found the methods too time-consuming and not sufficiently specific.

Goldstein has also prepared (32) a systematized procedure for the qualitative analysis of textile processing agents. The treatment appears comprehensive and well organized, but has not yet been tried by the present reviewers. Here again the scope may be too broad to permit the desired specificity.

Specific Methods. The following specific methods were proposed during the past two years and are not included in the general plans. Blout and Karplus give the infrared spectrum of polyvinyl alcohol. The spectrum (700 to 4000 cm.$^{-1}$) is displayed in graphs for dried films of polyvinyl alcohol of varying degrees of polymerization (12). Taat and van der Heul (95) have proposed a solvent fractionation method for the investigation of technical polyvinyl products, particularly polyvinyl chlorides. The polymer is dissolved in a specified boiling cut of technical o-dichlorbenzene, and the chloride, or chloride-acetate copolymer, is precipitated with alcohol. If the acetate is present as a mixture, it is precipitated from a predominantly acetone solution of the filtrate with water, leaving the plasticizer in the final filtrate. If pigments or fillers are present, they can be centrifuged from a solution of o-dichlorbenzene plus butanone as the initial separation step.

McGovern, Grim, and Teach (44) measure the proportion of the monomer in polystyrene by means of an ultraviolet spectrophotometer at 282 or 291 mμ, either directly or in solution. In the latter instance, methanol is used as solvent. Laitinen, Miller, and Parks (42) determined the ultraviolet absorption spectra of substituted vinyl aromatic monomers and polymers and collected data for a wide variety of substituted styrenes. The method has been used for the determination of monomer ratios in butadiene copolymers.

Tyler and Higuchi describe (97) the development of methods of chemical analysis of synthetic rubber and discuss the present status. They conclude with a list of analytical methods still needed. Not included in this review is a new method by Kolthoff, Lee, and Carr on the determination of polystyrene in GR-S rubber (39). The polymer containing C=C groups is broken into alcohol-soluble aldehyde fragments by the action of a hydroperoxide in the presence of osmium tetroxide. Unaffected polystyrene is weighed after oxidation and extraction of the rest of the polymer. Dinsmore and Smith discuss at length the analysis of natural and synthetic rubber by infrared spectroscopy (27).

For the identification of some nitrogen-containing synthetic resins, Kappelmeier describes methods for urea, thiourea, melamine, sulfonamide, and polyamide (36, 37). The urea resin method uses aniline or benzylamine to convert the urea to diphenylurea or dibenzylurea, respectively. The solid crystalline derivatives have characteristic melting points. By suitable modifications, the method can be made quantitative. Thiourea, melamine, and sulfonamide resins do not interfere. Melamine is converted to cyanuric acid with 45% orthophosphoric acid. Sulfonamide resins are detected by isolation of p-toluene sulfonamide on acidification of an alkaline solution of the resin. This method has been evaluated by the reviewers for urea and melamine with good results, both qualitative and quantitatively. The urea method, however, seems to be subject to certain interferences. For example, a urea-formaldehyde resin including furfural did not give a positive qualitative test for urea.

Pfeiffer (77) uses a procedure similar to the Kappelmeier aniline method for the identification of urea resins in wrinkle-proof fabrics containing 1 to 10% urea resin. With 5-gram fabric samples, at least 4% resin is needed to get enough crystals for a melting-point determination. Neither dyes nor melamine formaldehyde resins interfere. Bursztyn (18) in a study of the manner of deposition of amino-resin wet-strength additives for paper, uses a selective dye which is more intense than that used by Stafford, Thomas, Williams, and Woodberry. Bursztyn's results are illustrated by a series of colored photomicrographs of microtomed cross sections of the paper.

Widmer (105) has prepared a detailed discussion of the detection of melamine and urea resins in wet-strength paper which is a modification and amplification of the treatment by Stafford, Thomas, Williams, and Woodberry (93). Melamine is vacuum-sublimed from the extracted, hydrolyzed resin and identified microscopically as such and as the picrate. Urea is obtained as dixanthylurea, which is recrystallized from pyridine before microscopical identification. Marshall and Aulabaugh (49) locate melamine resin in treated wool fibers by using a specific dye and employing a microscope on thin cross sections of the fibers. Waltz and Taylor (100) discuss the determination of the molecular weight of nylon and give details of methods for titrating the proportion of end groups. Aelion and Lenormant (2) discuss the infrared absorption spectra of polyamides and the structure of polar groups.

E. G. Rochow allows a brief chapter of his book (83) for the quantitative analysis of silicones.

He describes the method of Hyde and deLong, which is a wet oxidation method using concentrated nitric and sulfuric acids, igniting, and weighing as silica. Rochow describes his own method for the simultaneous quantitative determination of carbon, hydrogen, and silicon in a combustion chain which is especially designed to oxidize volatile decomposition products and to avoid the formation of silicon carbide. The optimum temperature of combustion must be determined for each type of polymer. The combustion is deliberately slow, but three principal elements are determined at once. (No satisfactory determination of oxygen exists to date). The simplest and easiest method for halogens attached to silicon consists of hydrolyzing the sample in ice water and titrating the resulting hydrohalide acid with standard base. The method does not distinguish definitely between halogen-to-silicon and halogen-to-carbon linkages. Hydrogen attached to silicon is determined by measuring the hydrogen evolved by 30% sodium hydroxide. Hydroxyl groups are determined by the Grignard method. Nitrogen can be determined by the Kjeldahl method and silicon is determined simultaneously by filtering out and weighing the silica.

Wright (107) gives the infrared spectra of the cyclic methyl polysiloxanes. He lists data in the 2 to 14μ range, using carbon tetrachloride for the 2 to 7.5μ range and carbon disulfide for the 7 to 14μ range. He includes a description of the method of preparation of polymers for examination and a rough classification of the types of vibrations made in case of stronger bands.

Properties. The most extensive collection of practical properties of resins, plastics, and elastomers is given in the plastics

‚properties chart (68), which deals with some 38 types of resins, with spaces for values for 45 properties, most of them obtained by A.S.T.M. test methods as indicated. This chart is coordinated with an extensive chapter on methods of testing (57), which describes briefly the procedures involved (chiefly A.S.T.M.) and lists A.S.T.M. specifications for many types. Other technical data are given in another section (58). Many of these data can be of determinative use.

This material can be supplemented by a number of recent discussions of the properties of individual groups of high polymeric materials. Mack, in his discussion (45) of the selection and application of plastics, gives a general comprehensive treatment which includes tabulations of types and forms of plastics, chemical resistance, and physical properties of 45 types of plastics.

Articles discussing some of the properties of condensation resins include those of Connor on ethylcellulose (22), Kropa on the polyester resins (40), and Irish and Stirrat on silicone rubber (35). Kropa's general discussion includes x-ray diffraction patterns and dielectric properties; Irish and Stirrat have tabulated the average physical testing properties of silicone rubbers.

Articles on the properties of addition polymers include Bekkedahl's general summary of the properties of natural rubbers including refractive index, density, and several thermodynamic properties (7). Salomon and Koningsberger's (89) theoretical discussion of the properties of rubber-like high polymers is buttressed with empirical data on density, brittle point, softening point, etc. Somewhat more specific discussions include those of Freeth (29) and Maibauer and Myers (46) on the polyethylenes, Rothrock on the acrylics (86), and Waters on the methacrylates, including the physical properties of methyl, ethyl, propyl, butyl, and isobutyl methacrylate (103). Schildknecht, Zoss, and McKinley have compiled a good review on vinyl alkyl ethers including a tabulation of physical properties (90). Shackleton (91) lists the chemical and physical properties of Polythene, Lucite, nylon, and Teflon. Rugeley, Feild, and Fremon (87) in discussing Vinyon N resin and fibers, include viscosity, density, and heat behavior data for the resin, as well as solubility characteristics and a list of plasticizers.

OILS

The analysis of drying oils is discussed at length by Bradley and Kropa in their chapter (54) in the Mattiello series. Although the treatment includes detailed descriptions of a large number of physical and chemical procedures for oils before incorporation into the film, the authors are concerned hardly at all with dried oils or other applied coatings. The analyst of coated materials will, however, be interested in the Bradley and Kropa review of calculating specific refraction and molecular refraction and comparing the empirical molecular refraction with the theoretical value derived from the sum of the values for the structural groups. Such computations can be of value in determining structural relationships in polymers, using appropriate methods for determining the constants.

This chapter may be supplemented by a number of articles from the recent literature. André (3) in discussing the saponification value, includes its origin, determination, and relative error and considers deviations of the saponification values determined in different laboratories. Trillat (96) describes the application of x-rays to the study of fatty substances in a review of x-ray diffraction methods applied to paraffins, fatty acids, soaps, alcohols, esters, amides, fats, waxes, polymethylene derivatives, and ketones. Appell (4) describes the technique of chromatography as applied to the separation of unsaponifiable material, fatty oils, glycerol, and oxidation and polymerization products of oils. Burton and Byrne (19) give methods for determining the constitution of sulfated oils, including a detailed titrimetric method for the —COOH, —OSO$_2$OH, and —SO$_3$H groups and their salts. Breusch and Ulusoy (16) describe the isolation and identification of fatty acids as bis-(p-dimethyl-

aminophenol)-ureides. Fatty acids separate as ureides when ethereal solutions of fat mixtures are heated with the reagent. Melting points and solvent solubilities are listed for the saturated and unsaturated series. Gorbach and Malissa (33) use the microanalytical detection of oleic and linoleic acids in fats and oils. Oleic is oxidized to dihydroxystearic and linoleic to sativic acid. Details of separation and melting points are included as well as brief crystallographic descriptions.

Diemair and Schröder (26) have a new analytical method for the identification of synthetic fats by the perception of transient green-to-blue colors when furfural is slowly added to a carefully prepared solution. Piskur's annual reviews of the literature on fats, oils, and soaps (78) are also potential sources of additional data.

PIGMENTS

Three chapters of "Protective and Decorative Coatings," all with Vesce as an author, contain a wealth of analytical information about pigments. They would be even more valuable if gathered together and indexed for the analyst.

In Chapter 1, Volume II (51), Vesce and Ryan classify 331 pigments as colored, white, black, or metallic, and subdivide them into organic or inorganic and synthetic or natural. At the end of the description of each small family of pigments there are one or more (presumably) specific physical or chemical tests with references to the literature, often A.S.T.M. specifications.

In Chapter 4, Volume V (54), Vesce describes, according to their spectral reflectances, all the pigments that are classified in Chapter I. These spectral descriptions are intended to be used for determinative purposes before the specific tests mentioned above. There are two different procedures for measuring spectral characteristics between 400 and 900 mμ. One is to photograph a standardized briquet of the pigment under strictly specified photographic conditions by four specific bands of wave lengths. The four photographic negatives are compared with their respective set of standard negatives or their density is measured with a densitometer. The per cent reflectance for each band is arranged for 181 pigments in a table. The other (more expensive) method is to record the curve for reflectance versus wave length on a Hardy type of recording spectrophotometer. Curves are given for 200 pigments.

Chapter 3, Volume II (51), by Vesce deals with the microscopical identification of 34 azo dyes and organic pigments regardless of their metallic (cationic) radicals. This procedure involves adding the pigment, dry or in benzene solution, to a drop of concentrated sulfuric acid, or vice versa, on a microscope slide, and after a few minutes, observing the reaction product under a microscope at about 200 X. Identification is made by recognition of the crystalline habit which appears to be characteristic for each of the 34 species (provided that the conditions are kept constant).

Pratt (80) has three chapters (IX, X, and XI) of particular interest to the analyst of pigments. Although the author repeatedly contends that physical properties of pigments are as important as chemical ones, he distinguishes between analysis (chemical) and testing (physical). This distinction results in incomplete indexing of physical properties which are of great determinative value. Nevertheless, the persistent analyst will find a wealth of material, which will suggest a procedure for broadly classifying pigments.

The last of these determinative chapters deals with pigment types and properties and is so broad in its classification that it might well be considered first. It contains Doty's table (28) of physical-chemical properties which are intended to be evaluative for the formulator, but are just as valuable for identification purposes.

Chapter IX deals with the testing of pigments and describes briefly the determination of physical appearance, fineness, texture, moisture, specific gravity, and water-soluble matter. It also includes Doty's bleed tests (28) in water, oil, "lacquer" thinner, and "synthetic" (coal tar) thinner. There is a section on the use of the light microscope, particularly to identify derivatives whose particle size and shape are adequate. The limitation of the light microscope in the range of discrete pigment particles and the ad-

vantage of the higher resolving power of the electron microscope are brought out by Pratt and also by Sawyer (53). (Curiously enough, Pratt mentions only the electrostatic type of electron microscope proposed but never really commercially produced by the General Electric Company.) Pratt assigns a major role to x-ray and electron diffraction in the study of pigments. He also includes in this chapter on "testing" a variety of chemical tests: spot, chromatographic, capillary separation, dyeing, and "chemical." He describes the use of spectrochemical analysis for the qualitative and quantitative "estimate" and "analysis" of the inorganic elements in pigments, as well as reduction methods of separating and determining amino pigments. The phosphotungstic and phosphomolybdic pigments are determined (with difficulties) by means of their tungsten and molybdenum contents.

Chapter X, "Identification of Organic Pigments" (80), includes the determinations of melting point and those chemical tests already mentioned. It devotes much space to the system of Weisberg and Smith (104) with slight modifications by Pratt to extend the use to applied coatings. The system is based on a preliminary classification according to color and the subsequent use of common chemical reagents: dioxane, 20% sodium hydroxide, concentrated sulfuric acid, stannous chloride solution followed by hydrogen peroxide, hot dilute sodium hydroxide, and methyl alcoholic hydrochloric acid. He includes a description of the Hardy-type of spectrophotometer with only 18 curves of individual pigments by Abbott and Stearns (1).

The more recent periodical literature contains a number of articles of analytical interest on pigments and fillers. Moore (71) in discussing the application of crystallographic techniques to titanium pigments illustrates the value of crystal chemistry in the study of pigments and pigment-producing materials. Stead (94) reviews the effects of chemical composition, crystal form, particle size and shape, refractive index, specific gravity, and dispersion with surface agents for a representative group of pigments, and discusses methods of obtaining several of these characteristics during pigment manufacture. Sagristá (88) in reviewing fillers for paper, discusses the preparation and determination of kaolin, bentonite, talcum, asbestos, tripolite, barium sulfate, calcium carbonate, magnesium carbonate, zinc sulfide, and titanium dioxide.

WAXES

Two fairly recent books are sources of analytical information on natural and synthetic waxes. Warth (102) devotes a chapter to methods for determining the constants of waxes, the data serving as a means of identification, differentiation, or classification. The treatment is comprehensive and consists of detailed descriptions of a large number of chemical and physical methods, the results from most of which are scattered through the descriptions of the individual types of waxes. Bennett (10) includes a considerable amount of analytical information in a chapter on "wax technology" and, in addition, presents a detailed analytical scheme for the identification of mixed waxes.

The more recent literature includes two papers on wax analysis. Bigelow (11) briefly describes methods developed by Karl Fischer in Germany, comprising a data-plotting method which permits classification of waxes according to chemical characteristics, the detection of microscopic amounts of oil by certain dyes, a new electro-optical method for the determination of paraffin wax, and a method combining polarized light and dark-field illumination for studying the crystalline nature of waxes. Newberger (72) describes a chromatographic method for the analysis of mixtures of hydrocarbons, beeswax, and spermaceti. The description includes results based on typical separations.

SPECIFIC ANALYTICAL APPLICATIONS

Included in this section are a number of specific methods for some individual constituents of the coating materials thus far considered.

Elementary Analysis. Backeberg and Israelstam (5) describe a modification of the Epprecht and Hornung method for detecting nitrogen, sulfur, and halogens in organic compounds. Decomposition is effected with calcium oxide. The evolved fumes are

treated with Riegler's reagent and yield a *red color if nitrogen* is present. Sulfur is detected as hydrogen sulfide; chlorine as silver chloride. Velluz and Pesez (98) describe a micromethod for the detection of nitrogen in organic molecules in which the ammonia produced by the reaction is detected by the fluorescence it imparts to a neutral solution of zinc sulfate and oxine. The test is said to be applicable to nitro compounds.

Polyhydric Alcohols. Palfray, Sabetay, and Libmann (76) describe a new procedure for the determination of water and polyhydric alcohols by the use of various entraining agents. Refluxing with cyclohexane, using a Dean-Stark trap, entrains ethylene, trimethylene, and propylene glycol. Turpentine entrains these and, in addition, diethylene glycol and glycerol.

Newburger and Bruening (73) report on the estimation of glycerol in the presence of propylene and ethylene glycols, using a modification of the Shupe procedure, in which glycerol is oxidized with potassium periodate and the resulting formic acid is titrated. Pohle and Mehlenbacher (79) treat the analysis of mixtures of glycerol, propylene glycol, and trimethylene glycol. Glycerol is determined as formic acid after oxidation with periodic acid. Propylene glycol is measured by titration of the iodine which is liberated by the addition of potassium iodide to the oxidized solution. Trimethylene glycol is determined by its acetyl value. Fürst (31) describes a microchemical method for the colorimetric detection of glycerol in dilute aqueous solutions by condensation of the dehydration or oxidation products of glycerol with 2,7-naphthalenediol in concentrated sulfuric acid. Formaldehyde, acetaldehyde, acrolein, and other aldehydes interfere.

Aldehydes. Reynolds and Irwin (82) present a good critical discussion on the determination of formaldehyde and other aldehydes by gravimetric, colorimetric, potentiometric, and spectrographic methods. A tabulated synopsis of all the methods is included for quick reference. The review also includes the authors' selections for specific cases. Fürst (30) describes a color reaction with carbazole for the rapid and simple detection of formaldehyde. A sensitivity of 10 micrograms is claimed.

Dibasic Acids. Warshowsky, Elving, and Mandel (101) apply polarographic analysis to mixtures of maleic and fumaric acids. The method permits simultaneous determination of the acids or their salts, using an ammonium hydroxide–ammonium chloride buffer solution of pH 8.2 as supporting electrolyte. Acids can be separated from most interfering substances by precipitation of the barium salts from ethanol solution; the precipitate is soluble in the buffer. Boudet (13) discusses the identification of organic acids and nitrophenols by means of their benzylammonium salts. The method of Buehler et al. (17) is improved by using an excess of the acid and benzene as an inert solvent. The N-benzylamides of monocarboxylic acids are prepared without external heating; those of the dicarboxylic acids are prepared by briefly heating the acid with pure benzylamine. The reported melting points of the dicarboxylic acid amides do not agree well with those reported by Dermer and King (25).

Fatty Acids. Ramsey and Patterson (81) present a detailed description of the separation and determination of straight-chain saturated fatty acids, C_5 to C_{10}, by partition chromatography. Silicic acid is the adsorbent, methanol the immobile solvent, 2,2,4-trimethylpentane the mobile solvent, and bromocresol green the indicator.

Phenols. Kletz and Price (33) report the infrared spectra of twelve solid and liquid alkyl phenols in the 5 to 15μ wave-length range.

Rubber Compounding Ingredients. Bellamy, Lawrie, and Press (8, 9) treat the chromatographic analysis of rubber-compounding ingredients and their identification in vulcanizates and include general principles and methods, details of chromatographic separation of accelerators, identification by color reactions with metal salts, and details of the identification of antioxidants.

CONCLUSION

During the preparation of this brief survey, the reviewers observed with regret the relatively small number of papers of value to the analyst compared to the large number of data-free general discussions. It is encouraging to note, however, that the number and variety of useful papers are increasing—a prediction, it is hoped, of increasing interest in this rather neglected aspect of the field of coatings. It is true that there is no completely satisfactory method for the analysis of individual coating constituents. The solution to the problem presented by coatings in all their complexity may never be entirely realized, but increasing activity in the field is sure to culminate eventually in one or more general systems to serve as framework for the solution of individual problems.

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ESSENTIAL OILS AND RELATED PRODUCTS

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THE analysis of essential oils and related products is a highly specialized field of analytical chemistry. Because of the chemical complexity of these natural products, procedures must be standardized carefully to give reproducible results. As the analytical data obtained seldom represent actual percentages of single constituents, procedures that are but slightly modified may give very different results. Because of this fact, a new procedure is not accepted readily; those methods which are included in an official compendium such as the United States Pharmacopoeia or the National Formulary soon become firmly established.

In the field of research, new techniques and procedures are being employed for the isolation and identification of constituents of essential oils. At the present time, absorption and Raman spectra are used for proof of chemical identity and for elucidation of structure—e.g., irone. Chromatographic adsorption has been used for the isolation of individual constituents of essential oils—e.g., coumarins in expressed lime oil, azulenes, etc. At some later date, these techniques may be modified for the analysis and evaluation of oils, but thus far they have not been applied generally to analytical control.

Colorimetric determinations usually are not applicable to mixtures as complex as essential oils. Consequently, these determinations (as well as "color tests") are not considered here. This paper is restricted to a discussion of several important publications of interest to the essential oil chemist, and a report on analytical procedures that have been suggested or evaluated during 1945 to 1948, inclusive.

OFFICIAL COMPENDIA

In this four-year interval, new editions of several official compendia have appeared.

The Pharmacopoeia of the United States, thirteenth revision (*109*), became official on April 1, 1947 and was soon followed by two supplements. This revision contains specifications for eighteen essential oils and in addition some seventeen sundry items of interest to the essential oil trade—e.g., floral waters, isolates, balsams, and certain synthetics. Monographs are included for the following:

The specifications and methods of assay and analyses for these products were not changed materially from those of the preceding revision. Eight essential oils and two related synthetics which were official in the United States Pharmacopoeia, twelfth revision, do not appear in the thirteenth revision:

Essential oils
 Bitter almond oil
 Chenopodium oil
 Juniper oil
 Volatile oil of mustard
 Dwarf pine needle oil (oil of *Pinus*
  pumilio)
 Rectified tar oil
 Turpentine oil
 Rectified turpentine oil

Synthetics
    Allyl isothiocyanate
    Terpin hydrate

Benzyl benzoate became an official pharmacopoeial drug for the first time in this revision.

The National Formulary, eighth edition (*59*), also became official on April 1, 1947; one supplement has been issued since that date. Monographs are included for the following products:

This latest edition of the National Formulary included the ten items mentioned above, which no longer are official in the United States Pharmacopoeia, and new monographs for benzyl alcohol and pine oil. Necessary changes were made in several of the monographs to make them conform to the latest reliable data for products of high quality used as drugs. In the assays for benzaldehyde, bitter almond oil, and cinnamaldehyde, the Stillman-Reed method (*60*) was substituted for the hydroxylamine hydrochloride method formerly employed (*58*). Although the Stillman-Reed method was carefully checked and found to be satisfactory by Martin, Kelly, and Green of the American Pharmaceutical Association Laboratories (*50*), some difficulty in visually establishing the proper end point has been experienced. The use of a Beckman pH meter (to adjust the pH of the end point to 3.45) gives results that have proved satisfactory, but for a routine assay the method of the seventh edition of the National Formulary appears preferable. Furthermore, the hydroxylamine hydrochloride solution is stable, but the Stillman-Reed solution must be freshly prepared. Minor modifications in other assays have been made, in order to obtain better reproducibility and accuracy. In many of the monographs for essential oils, a new subheading, "Solubility in Alcohol," has been incorporated, this is to indicate that such datum is a specification of

purity for the oil, and to distinguish it from the supplementary, informative statements that appear under the subheading "Solubility," which has been retained.

The British Pharmacopoeia 1948 (*11*) replaced the 1932 edition and its seven addenda. Monographs are included for the following:

Three essential oils which were formerly official in the British Pharmacopoeia 1932 have not been included: oil of Siberian fir, oil of sandalwood (East Indian), and oil of sandalwood Australian. For most of the essential oils, specific gravity at 15.5° C. has been replaced with weight per ml. at 20° C. In other respects, the specifications and analytical procedures follow closely those of the 1932 edition.

The Dispensatory of the United States is closely associated with the three official compendia already discussed. A new edition, the twenty-fourth (*18*), appeared in 1947, based upon the latest United States Pharmacopoeia and National Formulary. However, this edition refers to the British Pharmacopoeia 1932 and its seven addenda, as the Dispensatory was published before the appearance of the British Pharmacopoeia 1948. Many essential oils and related products which are not official are also included in this volume; these appear in the second section of the Dispensatory.

Another official volume which was published during this period is the sixth edition of the Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists (*5*). Under the heading "oil of chenopodium" (p. 735) appears a detailed procedure for the determination of ascaridole by the titanium trichloride method. The analysis of flavoring extracts is adequately covered (*5*, pp. 365-80).

NEW TEXTS AND PUBLICATIONS

During the period 1945-48, several important works have been published which contain chapters on the analysis of essential oils and related products.

In 1948 appeared the first volume of a new series dealing with essential oils by Ernest Guenther, "The Essential Oils" (*33*). In Volume I may be found an entire section devoted to the methods of analyses used commercially in this field. Detailed procedures are given, as well as a discussion of the significance and limitation of many of the tests. Physical and chemical methods of analysis are described, and procedures for the detection of adulterants and other special tests are given. The chapter on examination and analysis of essential oils, synthetics, and isolates, written by Edward E. Langenau, covers some 140 pages.

In 1947 there appeared the first English translation by E. Sagarin of the well-known French work of Naves and Mazuyer, "Natural Perfume Materials" (*81*). This is actually a partial revision of the original work: many additional data have been included by the translator in order to bring the work up to date. Here may be found established methods for examination and analyses of concretes, absolutes, resinoids, and similar natural floral products.

In 1948, Schimmel & Co. issued a report (*96*) covering the year 1945. The return of this well-known brochure is welcomed by all chemists interested in essential oils.

A noteworthy step toward the standardization of analytical procedures and the maintenance of high quality is to be found in the specifications and standards of the Essential Oil Association of the United States (*25*). The Scientific Committee of this body has drawn up specifications for the best grade of material commercially available.

Procedures for the determinations and assays are given in "E.O.A. No. 1, Determinations"; modifications, when necessary, are given in the individual monographs. This ambitious program was begun in 1946 and will be continued. The following standards and specifications have been approved by the membership of the Essential Oil Association and published in loose-leaf form:

> Essential oils
> Oil of bois de rose Brazilian
> Oil of cajuput
> Oil of cedarwood
> Oil of citronella Ceylon
> Oil of citronella, Java type
> Oil of copaiba
> Oil of ginger
> Oil of grapefruit
> Oil of lemongrass (East Indian and West Indian)
> Oil of palmarosa
> Oil of patchouly
> Oil of petitgrain Paraguay
> Oil of spike
> Oil of spruce
> Oil of vetiver
>
> Synthetics and isolates
> Aldehyde C-10
> Amyl salicylate
> Benzyl acetate
> Cinnamic alcohol
> Citral pure
> Citronellol
> Dimethyl anthranilate
> Geraniol
> Geranyl acetate
> Heliotropin
> Hydroxycitronellal
> Indol
> Linalyl acetate
> Methyl anthranilate
> Nitro musks
> Phenyl acetic acid
> Phenyl ethyl alcohol
> Safrole
> Terpineol
> Terpinyl acetate

Two new periodicals deserve special attention: *Analytica Chimica Acta* (*1*), Vol. I, No. 1, of which appeared in January 1947; and *Industrie de la Parfumerie* (*39*), first appearing in April 1946.

ANALYTICAL PROCEDURES FROM THE SCIENTIFIC AND TECHNICAL LITERATURE

Acids. Ekwall and Juup (*23*) described a potentiometric precipitation titration of the saturated fatty acids, C_{12}, C_{14}, and C_{16}, with silver nitrate; the application of potentiometric titration to the well-known "fractional precipitation" of acids could profitably be extended and should be thoroughly investigated. Mouratoff (*55*) reported on a method for the characterization and separation of lower fatty acids by entrainment with steam; the principle is similar to that of the Dujardin-Salleron method for the determination of volatile acids in wine Ramsey and Patterson (*92*) described in detail a technique for the microseparation and identification of the C_1, C_2, C , and C_4 acids based on a chromatographic method; butyric and isobutyric acids were not separated from each other, but were obtained together as a mixture. These authors (*93*) also studied the separation of the straight-chain saturated acids, C_5 to C_{10}, by the same method. In a later study, Ramsey (*91*) suggested a further chromatographic partition method for the separation of butyric and isobutyric acids.

Pagel and McLafferty (*84*) recommended the use of tributyl phosphate for extracting organic acids from aqueous solutions; they showed this solvent to be more effective than ethyl ether, isopropyl ether, benzene, toluene, or chloroform for the extraction of short-chain aliphatic acids.

Alcohols and Phenols. Terent'ev and his collaborators (*106–108*) investigated the determination of active hydrogen by means of a Grignard reagent in an atmosphere of carbon dioxide; most alcohols, glycols, phenols, and acids gave satisfactory results, but tertiary alcohols which easily split off water gave high values. These authors found the following solvents satisfactory for this determination: ether, benzene, xylene, chloroform, and dichloroethane; methyl magnesium iodide gave better results than methyl magnesium bromide when used with anhydrous ether. Lehman and Basch (*45*) found dibutyl ether to be a good solvent for this determination; they report that pyridine proved unsatisfactory and that methane as an inert atmosphere offered certain advantages over carbon dioxide.

Palfray, Sabetay, and Libmann-Métayer (*47, 53, 87, 88*) described a selective entrainment procedure as a new method for the separation and determination of polyhydroxylic alcohols. Ogg, Porter, and Willits (*82*) reported on the determination of the hydroxyl content of organic compounds by means of a 1 to 3 acetic anhydride–pyridine mixture; the excess anhydride is hydrolyzed, butyl alcohol is added as solvent, and the acetic acid formed is titrated potentiometrically to a pH of 9.8. Jones and Fang (*41*) described the determination of menthol in peppermint oil by the use of this reagent; they stressed importance of running a blank. Naves (*69*) evaluated a modification of this acetic anhydride–pyridine method as applied to alcohols found in essential oils. He reported that the procedure was satisfactory for primary alcohols; secondary alcohols were 93 to 97% acetylated under conditions that gave quantitative values for primary alcohols; tertiary alcohols were acetylated only to the extent of 5 to 10%; aldehydes interfered but slightly. In a later publication, Naves (*71*) suggested heating the mixture at 100° C. for 15 minutes to determine primary alcohols, and for 3 hours at 100° (or for 15 minutes at 140°) to determine primary plus secondary alcohols.

For the estimation of primary and secondary alcohols, Elving and Warshowsky (*24*) recommended the use of phthalic anhydride–pyridine reagent, and heating the mixture for 1 hour at 100° in a pressure bottle; tertiary alcohols and phenols do not

interfere. Naves (66) showed that in the determination of alcohols in essential oils by accelerated acetylation techniques—i.e., addition of sulfuric or phosphoric acid as catalyst—the presence of cineole in the oil will give rise to inaccuracies, since this oxide is converted into a mixture containing terpinyl acetate and terpinol diacetate. Palfray, Sabetay, and Garry (86) again have suggested the use of sodamide for the determination of tertiary alcohols; the evolved ammonia is collected and determined. Naves (67) studied three well-known methods for the determination of tertiary alcohols: the method of Schyver (97) using sodamide; the method of Tschugaeff and Zerevitinov (114, 115) using a Grignard reagent; and the modification of Soltys (102). Satisfactory results were obtained with the last procedure if the oils were thoroughly dried and then dissolved in benzene (or other hydrocarbon solvent) and permitted to react for 30 minutes; primary, secondary, and tertiary alcohols and phenols react to give values between 99 and 102% of the theoretical. Duke and Witman (20) suggested a potassium permanganate oxidation technique for the identification of primary and secondary alcohols; the corresponding aldehydes and ketones are identified by conversion to the 2,4-dinitrophenylhydrazones. For the identification of citronellol in the presence of geraniol and nerol, Naves (70) proposed hydrogenation in ethyl acetate at 60° over a platinum oxide catalyst; under these conditions, citronellol yields the corresponding dihydro alcohol, but geraniol and nerol are converted to the hydrocarbon dimethyloctane. Naves (64) reported that formylation was found to be suitable for the determination of borneol and 3-octanol in oils which also contain linalool and its esters (the tertiary alcohol being dehydrated); however, if benzyl alcohol or benzyl acetate is present, some of the benzyl formate which is formed will be lost in the subsequent washing with saturated sodium chloride solution; this author maintains that better results will be obtained if 90% formic acid is used in place of the 98% (or 86%) acid often recommended. Naves (68) reported that, contrary to statements made by other investigators, the ionones do not yield esters when treated with the acetic anhydride–formic acid mixtures used for the estimation of alcohols in essential oils.

In a study of the determination of the hydroxyl number of cetyl alcohol, Green (31) reported that the National Formulary procedure (61) proved more convenient than the method of the Association of Official Agricultural Chemists (4); furthermore, the results were more concordant. Waters and Beal (113) pointed out that the melting point of racemic synthetic menthol is a poor criterion of purity; the double congealing point, however, is an excellent test. Naves (73) presented a critical review of the methods employed for the estimation of alcohols in essential oils (15 references). Gengrinovich (29) suggested the use of a solution of iodine chloride in hydrochloric acid for the direct titration of certain phenols; starch was used as an indicator.

Aldehydes. Clark, Kaye, and Parks (14) described the advantages of the use of x-ray diffraction data for the identification of aldehydes and ketones as 2,4-dinitrophenylhydrazones; as little as 1 microgram of material can be identified, or even a single crystal; data are presented for some 21 aldehydes and ketones. Roberts and Green (94) reported on the separation of 2,4-dinitrophenylhydrazones of several aldehydes and ketones by chromatographic adsorption using a column packed with a mixture of silicic acid and Supercel (2 to 1). Langlais and Bollinger (44) reported a new method for the determination of aldehydes by measuring the amount of water produced by the condensation with aniline [a modified Dean and Stark (17) apparatus is employed]. Because ketones react slowly they do not interfere appreciably; furthermore, upon addition of aluminum chloride ketones also react, permitting a separate determination of these two types of carbonyl compounds. It would appear that this method does not offer much promise for analytical evaluation of essential oils as such.

Siggia and Maxcy (99) suggested a modified bisulfite method

for the determination of aldehydes; sodium sulfite and sulfuric acid are added to the aldehyde and the excess is titrated potentiometrically with sodium hydroxide to a pH characteristic of the individual aldehyde. Much further work would be required before this method could be applied generally. Hoffman (36) made a comparative study of methods for the determination of citronellal in the oil of *Eucalyptus citriodora:* The phenylhydrazine method of Kleber (42) gave higher values than the hydroxylamine method (three modifications); however, none of these methods proved entirely satisfactory; an exact determination for citronellal has yet to be published. Methods for the assay of preparations containing vanillin were discussed by Guevara (34), and microchemical procedures for the identification of vanillin and bourbonal were published by Rutten (95) and by Fischer and Kocher (27).

Esters. For the determination of the saponification equivalent of high boiling esters, Maglio (48) described in detail a modification of the technique employing diethylene glycol as solvent; 15 minutes' heating at 125° proved sufficient. This is an excellent method for difficultly saponifiable esters. Stuart (103) improved the apparatus of Matchett and Levine (51) for the determination of acetyl groups by transesterification; acetyl groups attached to an oxygen atom require about 2 hours for completion of the reaction; acetyl groups attached to a nitrogen atom require various periods of time depending upon the substitution present and other factors. André and Kogane-Charles (2) found excellent agreement among the three standard procedures for the determination of allyl isothiocyanate in mustard seed: argentimetric, iodometric, and gravimetric. These authors (3) report that the same methods do not give concordant results when applied to crotonyl isothiocyanate in rape seed: they express the opinion that the iodometric method is probably most correct. Lemieux and Purves (46) recommended a modification of the method of Kuhn and L'Orsa (43) for the estimation as acetic acid of acetyl, ethylidene, ethoxy, and α-hydroxyethyl groups; this method is based on oxidation with 30% chromium trioxide solution, the acetic acid formed being distilled off and titrated. Such drastic treatment prohibits the application of this method to essential oils as such.

Ethers. Houghton (37) described a micromethod for the determination of mixed methoxy-ethoxy groups; the ratio of methyl iodide to ethyl iodide obtained is established by a determination of density or boiling point. Fujita and Yamashita (28) introduced a method (38) applicable to essential oils for the determination of safrole as the mercurioxychloride addition compound. Shukis and Wachs (98) used this method to determine the amount of safrole in various mixtures; after determining the congealing points of these mixtures, a curve was prepared showing the relationship of safrole content to the congealing point. For the estimation of anethole, Mori (54) recommended an iodine absorption technique. The presence in an essential oil of other substances capable of absorbing iodine would appear to limit the use of this method.

Peroxides. Methods for the determination of organic peroxides were described by Tanner and Brown (104), Skellon and Wills (101), and Skellon and Thurston (100). Wagner and his collaborators (112) evaluated a modified iodometric method and also the thiocyanate (111) method for peroxide estimation; the reader is referred to the original paper for their detailed findings. (The determination of small amounts of peroxides in citrus oils has long been considered an evaluative procedure for detecting spoilage.) Halpern (35) reviewed the methods found in the literature for the determination of ascaridole in oil of chenopodium and pointed out their faults; the oxidation of ascorbic acid by ascaridole has been studied but found unsatisfactory for an analytical procedure. The procedure of the National Formulary (62) in spite of its admitted faults, still appears to be the most reliable method published thus far.

Terpenes. Putnam, Moss, and Hall (*90*) recommended the use of chloromaleic anhydride for the determination of conjugated diolefins. This modification of the Diels-Alder procedure offers the advantage of obtaining an adduct that contains an active chlorine atom; this chlorine can then be determined by an argentimetric procedure, the vinyl chlorine of the excess reagent remaining unreactive. The use of maleic anhydride addition numbers deserves greater recognition for the evaluation of essential oils. Marie, Dupont, and Dulou (*49*) proposed two methods for the determination of camphene in mixtures containing pinene; the methods may prove useful, but only if the mixture under investigation contains no terpenes other than pinene and camphene. Ipatieff, Thompson, and Pines (*40*) suggest the use of ethyl alcohol as a solvent for the potassium permanganate test for the detection of unsaturation; 96% (or absolute) alcohol was found more satisfactory than acetone.

Determination of Essential Oil Content. Bauer and Pohloudek (*8*) reviewed methods that employ steam distillation for the determination of essential oil content. Curl (*16*) made a comparative study of the several types of apparatus employed for the determination of volatile oil in citrus juices; for this purpose the McKinnis apparatus (which employs a 0.4-ml. microburet as a receiver) is entirely satisfactory, provided that a few drops of a wetting agent are used to wash down the condenser at the end of the distillation. Bartholomew and Sinclair (*7*) describe in detail a modified apparatus and technique for the determination of volatile citrus oils by a steam-distillation method. Burdick and Allen (*12*) suggested a distillation technique employing acetone and steam to give a rapid determination (about 7 minutes) of citrus oils in juice; results are comparable to those obtained in the slower Clevenger (*15*) method. In spite of the numerous modifications that have been suggested, the Clevenger method remains the most reliable and satisfactory for routine analyses; it is official in the United States Pharmacopoeia, thirteenth revision (*110*), the National Formulary, eighth edition (*63*), and the Association of Official Agricultural Chemists, sixth edition (*6*).

Naves (*65*) has pointed out that the analytical separation of essential oils from aqueous distillates is frequently incomplete because of the presence of water-soluble constituents; even after "salting out," extractions with a pentane–ethyl ether mixture may be necessary and prove preferable to extractions with pentane alone, especially if benzyl alcohol is present. Naves stated that the technique of codistillation with glycols requires revision in view of these considerations. In another article, Naves (*75*) again stressed the value of the determination of essential oil content and of properties of the distillate obtained with superheated steam at reduced pressures. This procedure is of much value in the evaluation of natural perfume materials such as floral absolutes and concretes.

Optical Methods (Refractive Index and Optical Rotation). Palfray (*85*) reported on the refractive indexes of certain perfume concretes; determinations were made upon the liquefied material at elevated temperatures (61° to 74° C.). Naves (*72*) pointed out the advantages obtainable from the use of refractive dispersion for the analysis of essential oils, and (*74*) reported values for the rotatory dispersion of citronellol, citronellal, and citronellic acid. Gilby and Igolen (*30*) criticized the values given by Naves and Angla (*78*) in 1941 for optical rotatory power of lavender oils; experience with 50,000 kg. of oil in 1942 indicated that the limits set by Naves and Angla are too narrow and consequently their method for detecting adulteration is unreliable. A reply to this criticism was given by Naves and Angla (*80*). The importance of the accumulation of sufficient data is evident here.

Detection of Adulterants. Naves (*76*) pointed out that the adulteration of essential oils still flourishes. The crude adulteration of the past is seldom encountered today; adulteration is becoming more scientific and more difficult to detect and to prove. Oschmann (*83*) stated that in the detection of phthalic acid, the acid must be identified with certainty, as other dibasic acids frequently may give deceptive positive tests. Although his work was not directly concerned with essential oils, its application to adulteration with phthalic esters is obvious. Naves (*77*) reviewed methods of detecting adulteration of lavender oil (especially with lavandin oil); the measurement of the dispersion of optical rotatory power for solutions of the oil in different solvents appears to offer a very promising method. The accumulation of more analytical data is indicated, before this method can attain practical significance. Naves and Angla (*79*) discussed the detection of adulterants with special reference to lavender oil and geranium oil; as routine analyses detect only gross adulteration, more specialized tests must be performed. There is some advantage in increasing the number of determinations performed, and in the isolation and identification of certain constituents; specialized methods must frequently be employed.

Cabrera (*13*) describes a new method for the determination of castor oil as an adulterant in essential oils; the test is based on the insolubility of castor oil in petroleum fractions. The procedure as described must be applied with discretion. The British technical press has publicized the so-called "London test" (*9*, *89*) for the detection of petroleum fractions in Ceylon citronella oils; like the Schimmel test, it is based on the behavior of the oil when diluted with 80% alcohol. For the actual proof of added mineral spirits, however, the analyst must resort to the well-known oleum test.

Miscellaneous. The heavy metals test of the United States Pharmacopoeia, thirteenth revision, was carefully evaluated by Bundy and Edman (*21*, *22*), whose findings indicate that the test leaves much to be desired in respect to accuracy and reproducibility if the amounts of heavy metals present are small. The test is satisfactory for values of the order of 20 p.p.m. This degree of sensitivity appears to be sufficient in the case of essential oils which are used only in minute amounts in the finished product. Greene (*32*) reported on the appearance and behavior of cassia and cinnamon oils when treated with various reagents; photomicrographs and drawings of the crystals that result appear in the original article.

Bose and Bhattacharya (*10*) described in detail the removal of chlorophyll from extracts of plant material; lead acetate is added to the extract and precipitated with hydrogen sulfide, and the lead sulfide which is formed adsorbs the chlorophyll. The amount of lead acetate required varies, but an amount corresponding to 9% of the plant substance in the extract is always sufficient. This method should prove of help in the investigation of plant extracts, where the presence of chlorophyll has often interfered with other determinations because of its color. Tarnutzer, Rittschof, and Boruff (*105*) presented absorption spectra data for juniper berry oil of various origins, orange oil, and coriander oil; the presence of dicarbonyl compounds (indicating oxidation of the oils) can be discovered. An accumulation of much data will be necessary before absorption spectra can be applied to routine testing of oils. Etinger and Baron (*26*) suggested the use of surface tensiometry as an assay method for pharmaceuticals (in particular, inorganic acetates). Measurements of surface tension might well be of value when applied to essential oils, their fractions, and related compounds; investigations undertaken in 1930 and 1932 by Müller (*56*, *57*) indicate that the use of this physical property has much promise. Maurel (*52*) published a paper dealing with the analysis and constitution of orange flower water; the determination of methyl anthranilate and indole is of much importance for the evaluation of this product. Dortan-Sontag (*19*) prepared a brief article dealing with established procedures for the analytical control of essential oils and their constituents.

During the past four years, considerable progress has been made in the analysis of essential oils and related products through the application of modern methods. Before these procedures

can be adopted for practical use, however, they must be applied to a large number of samples for final evaluation.

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FERTILIZERS

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UNTIL about 1920 the fertilizer-control chemist was chiefly concerned with determinations of moisture, nitrogen, phosphorus, and potassium and, aside from certain procedures for liming materials, these were the only fertilizer constituents for which official methods of analysis had been adopted in the United States (9). At present, however, the Association of Official Agricultural Chemists recognizes methods for no less than eight additional elements and for acid- or base-forming quality (14). Thus, boron was added to the list in 1925 (10), chlorine in 1930 (11), magnesium and acid- or base-forming quality in 1935 (12), calcium, copper, and manganese in 1940 (13), and sulfur and zinc in 1945 (14). Further additions will undoubtedly be made as time goes on (23, 270).

The literature of fertilizer analysis is scattered through many publications but the most fruitful sources of information in this field are ANALYTICAL CHEMISTRY, the *Journal of the Association of Official Agricultural Chemists*, and the association's "Methods of Analysis" (9–14) which is revised at 5-year intervals. Improvement of methods of fertilizer analysis has been a major objective of the A.O.A.C. since its foundation in 1884. From time to time the Association of Florida Phosphate Mining Chemists issues revisions of the methods used by that organization for analysis of phosphate rock (8). The present paper reviews developments in the analytical chemistry of fertilizers chiefly since 1943.

SAMPLING AND SAMPLE PREPARATION

Proper sampling is of major importance in fertilizer analysis (53, 273). The problem has been studied by Ross and co-workers (236) and more recently by Allen (4) who reports (1) that analyses of samples taken from bags with single-core and double-core tubes were in good agreement whether the bags were sampled in the horizontal or vertical position and (2) that serious loss of moisture may occur from samples stored in paper containers even for a few days.

Studies of sample preparation for analysis indicate that grinding to pass 20-mesh and 35-mesh sieves is usually satisfactory for moist and dry fertilizer mixtures, respectively (238). Dry samples, even of hygroscopic materials on humid days, are easily ground, with little loss of sample, in laboratory hammer mills of the types now on the market (235).

MOISTURE

Determination of moisture in fertilizers, which is complicated by the diverse nature of the materials, involves questions of easily volatile compounds, oxidation of organic matter, and decomposition of salts, resulting in loss of combined water and other substances. Whittaker and Ross (290) discuss the various procedures for moisture and their applicability to fertilizers. They suggest a method that involves drawing air through the sample at a constant, relatively low temperature (60° C.). This method (102, 110, 111), as well as vacuum drying over anhydrous magnesium perchlorate at room temperature, offers considerable promise for routine determination of free water in a wide variety of fertilizer materials and mixtures (102, 111, 237), including ammonium nitrate (237). Other recently proposed methods for moisture in ammonium nitrate and its melts are based on the rate of change in weight of the salt at 119° C. (98) and on the concentration–boiling point relationships of the melt under reduced pressures (301).

Yee (299) describes a rapid method for determining the hygroscopicity of fertilizers by measuring with an electric hygrometer the relative humidity of the air in equilibrium with the fertilizer. A procedure and apparatus for accelerated determination of moisture absorption by fertilizers are described by Yee and Davis (300).

NITROGEN

Most of the commonly used methods for nitrogen in fertilizers, as, for example, the Kjeldahl-Gunning-Arnold procedure, the development of which is outlined by Vickery (282), involve its conversion to ammonia which is distilled and determined titrimetrically. In the case of organic materials the conversion is ordinarily accomplished with sulfuric acid in the presence of a catalyst, usually copper sulfate or mercuric oxide. Recent investigations (214, 287, 288) further demonstrate the usefulness of these two catalysts.

Much attention has recently been given to the use of selenium and its compounds (24, 48, 55, 62, 130, 131, 136, 184, 199, 202, 205, 206, 211, 226, 253), alone or in combination with other catalysts, which effect more rapid oxidation of the organic matter and shorten the digestion time but may cause some loss of nitrogen if the digestion is unduly prolonged (62, 202). Better recovery of the nitrogen is said to be obtained with combinations of selenium and mercuric oxide (55, 202), and the selenates of copper, cadmium, and calcium, in the decreasing order, are reported to be more efficient than elemental selenium (62). The work on selenium catalysis is reviewed by Seebold (253).

Pepkowitz and co-workers (205, 206) favor the use of a small quantity of perchloric acid in the sulfuric acid–selenium digestion, and they describe rapid procedures that overcome the erratic results obtained with perchloric acid by other workers (291). Jonnard (130) recommends substitution of hydriodic acid for perchloric acid in the Pepkowitz method (205). White and Secor (287) report, however, that with mercuric oxide as the catalyst, pretreatment of the sample with hydriodic acid and red phosphorus as prescribed by Pregl and Roth (215, p. 89) does not give better results.

Sarudi (246) proposes digestion of the sample with sulfuric acid and 30% hydrogen peroxide without addition of a metal catalyst and alkali sulfate—a rapid procedure which, with certain modification (159), is said to give results in agreement with those obtained by the standard methods. Poe and Lane (211) report that use of hydrogen peroxide in connection with a mercuric oxide–selenium–copper sulfate catalyst further reduces the digestion time, but probably not enough to justify the additional trouble and expense. Other aids to the sulfuric acid digestion include potassium persulfate (17, 130), phosphoric acid (17, 211), dipotassium phosphate (211), and mixtures of dipotassium phosphate and ferric sulfate (216).

Marcali and Rieman (174) propose a novel, rapid procedure for nitrogen in organic materials which dispenses with the distillation step and, as modified (173), is applicable in the presence of phosphate, calcium, barium, iron, and aluminum. The method involves the usual digestion with sulfuric acid, potassium sulfate, and a mercury catalyst; addition of sodium bromide and zirconyl chloride; neutralization to the methyl red end point, with subsequent filtration; and titration with standard alkali in the presence of formaldehyde.

Shuey (260) points out that nitrogen is lost, presumably as nitrosyl chloride, when fertilizers high in nitrate and chloride are

analyzed for total nitrogen by procedures that involve reduction of the nitrate with the aid of salicylic acid (*14*, pp. 27–8). In the absence of organic nitrogen materials he recommends that the nitrogen be determined by the Devarda method (*14*, p. 28). For samples that also contain organic nitrogen he proposes a rather tedious combination of the Devarda and sulfuric-salicylic acid procedures; a more simple method for such samples, also involving the Devarda procedure, ·was developed by Dyer and Hamence (*70*) some years ago.

Aside from Shuey's work (*260*), use of the Devarda procedure for the analysis of materials in which the nitrogen is present only as nitrate or as ammonia and nitrate has recently been studied by several investigators (*33, 65, 76, 138, 163, 185, 217, 280*). Brabson and Karchmer (*33*) and Drouineau and Gouny (*65*) report that in the successive determination of ammonia and nitrate in a single sample, by distillation of the ammonia with sodium hydroxide and subsequent reduction of the nitrate with Devarda's alloy, low values for nitrate may be obtained as a result of interference by silica dissolved from the flask during the initial ammonia distillation; ways of overcoming this difficulty are outlined.

Wyatt (*296*) discusses possible sources of error in the Jones-Robertson method for nitrate nitrogen (*14*, p. 29) and suggests a modified procedure whereby more dependable results are obtained on mixed fertilizers. A new method for determination of nitrate involves its reduction to ammonia by means of ferrous sulfate and sodium hydroxide in the presence of silver sulfate (*58, 134*). Leithe (*156–158*) proposes to determine nitrate by treating the sample with standard ferrous sulfate solution and titrating with potassium permanganate or with potassium dichromate in the presence of phosphoric acid and ferroin.

A convenient but not highly accurate method for determination of nitrogen in ammonium sulfate comprises titration of the sample with sodium hypochlorite in the presence of disodium phosphate and potassium bromide (*42*). For the analysis of ammonium sulfate and other ammonium salts, Nicolas (*196*) recommends use of an apparatus that has been employed for determining nitrogen in steel. Miller (*185*) points out that titration with sodium hydroxide in the presence of formaldehyde is the accepted method for determination of total nitrogen in ordnance-grade ammonium nitrate, and he presents data showing that this rapid method is equally satisfactory for the fertilizer-grade material. Etheredge (*76*) reports good results by the formaldehyde procedure in a collaborative study of various methods for total nitrogen in ammonium nitrate.

In procedures involving distillation, absorption of the ammonia in boric acid—a little used practice in fertilizer analysis—has the advantage that it permits direct titration of the ammonia with a strong acid in the presence of a suitable indicator—bromocresol green (*283*), methyl red (*272*), or mixtures of methyl red and bromocresol green (*55, 136, 165*) or methylene blue (*54*). On the basis of a collaborative study with these indicators, Vignau (*283*) reports that bromocresol green gives the best results, both in the precision attained by each analyst and the agreement among them. Ballentine and Gregg (*17*) recommend absorption of the ammonia in potassium biiodate solution and titration of the liberated iodine. Regardless of the nature of the absorbent, efficient contact of the distillation gases with the absorbing medium is especially important in the analysis of high-nitrogen materials such as ammonium nitrate (*217*).

Improved apparatus and techniques in nitrogen determination have been devised. These include a manifold for disposal of fumes evolved during the Kjeldahl digestion (*276*); use of stearic acid as an antifoaming agent (*99*); simple devices to prevent bumping in distillations (*88, 108*); connecting bulbs (*163, 280, 294*); an ammonia trap (*213*); and a device for calculating nitrogen results (*148*). Distillation of Kjeldahl ammonia in closed systems is proposed by several workers (*25, 35, 45, 181*) and steam distillation in open systems by others (*120, 284*).

Although fertilizer analysts are seldom confronted with conditions that require or favor the use of micro- or semimicromethods and techniques for nitrogen, such procedures are receiving much attention (*17, 25, 54, 55, 120, 130, 136, 138, 153, 179, 184, 199, 206, 272, 287, 288*).

PHOSPHORUS

Among its other analytical uses, perchloric acid is finding increasing application as an aid to the digestion of samples containing siliceous and natural organic substances such as those commonly present in many phosphatic fertilizers (*18, 39, 93, 155, 171*). Thus, for the avoidance of difficulties arising from formation of gelatinous silica when solutions of basic slag are prepared by the customary hydrochloric-nitric acid procedure, Hardin favors digestion of the sample with mixtures of perchloric and nitric acids (*128*), while McNutt uses perchloric and hydrofluoric acids (*128*). Kassner and co-workers (*135*) recommend nitric-perchloric acid digestion for phosphate rock. Very low values for phosphorus in cottonseed meal and other oilseed residues are obtained on samples digested with nitric-hydrochloric acid mixtures (*6, 115*). Allen and Gault (*6*) report satisfactory results, perhaps slightly low in some instances, when such materials are digested first with nitric acid, and then with 70% perchloric acid. As compared with sulfuric acid digestion—also an effective means of bringing the sample into solution—the latter procedure has the advantage that it avoids introduction of the sulfate ion which is a disturbing factor in the volumetric determination of phosphorus by the molybdate method. As with sulfuric acid digestion (*113*, p. 558), there is evidence that some loss of phosphorus, presumably by volatilization, may occur when phosphatic materials are heated with perchloric acid at high temperatures or to complete expulsion of the acid (*128, 169, 222*). According to Bolin and Stamberg (*29*) the presence of a little sodium molybdate in the perchloric-sulfuric acid digestion shortens the time required for destroying organic matter, and has no undesirable effect on the subsequent colorimetric determination of the phosphorus.

Although gravimetric determination of phosphorus customarily involves its precipitation as magnesium ammonium phosphate hexahydrate and weighing as the pyrophosphate, MacKenzie and Dean (*171*) show that satisfactory results can be obtained by weighing the hexahydrate directly. Uncles and Smith (*277*) report that the presence of other salts, especially ammonium molybdate and oxalate, increases the solubility of the hexahydrate but with large additions of ammonium hydroxide, as in the analytical solutions of both phosphate and magnesium, the solubility is reduced to insignificance. This confirms the previous findings of Epperson (*74*) and Hoffman and Lundell (*116*). To avoid loss of ammonia and water the hexahydrate should be precipitated in the cold and dried below 30° C. (*68, 129*). The factors affecting the precipitation of the hexahydrate have also been studied by Lassieur (*153*). According to Schuhecker (*250*) and Lustig (*164*) elimination of carbon during ignition of the hexahydrate to the pyrophosphate is facilitated by ashing with the aid of perchloric and nitric acids. The change to pyrophosphate occurs at 477° C. (*68*).

Nydahl (*197*) and Thistlethwaite (*271*) verify the formula (NH₄)₃PO₄.12MoO₃ for ammonium phosphomolybdate, and the latter outlines a method for weighing the phosphorus as this compound.

The volumetric ammonium phosphomolybdate procedure is the most widely used method of determining phosphorus in fertilizers and fertilizer materials. The possibility of error in the method as a result of entrainment of hydrated molybdic acid in the phosphomolybdate is pointed out by Pannetier (*201*). Interference of the sulfate ion, which is present in the analytical solutions of many fertilizers and which causes high results when the phosphomolybdate is precipitated at elevated temperatures, can be largely avoided by making the precipitation at 25° to

30° C. with subsequent continuous agitation for an appropriate time (3; 14, p. 23; 28, 126, 233, 259). As shown by Richardson (227) and others (36, 126), sulfate interference in the hot precipitation procedure can be substantially eliminated by adding barium chloride or nitrate immediately after completion of the acid digestion of the sample; this modification, not recommended for solutions containing very large quantities of sulfate—such as those prepared with the aid of sulfuric acid (6, 126)—was officially adopted as an alternative procedure in October 1948. Although removal of the sulfate in this manner may lead to some loss of phosphorus in the form of insoluble sulfate-phosphate complexes (209), this appears to be of little or no consequence in practice. The work of Kassner, Crammer, and Ozier (135) indicates that the accuracy of the method is improved by precipitating the phosphomolybdate at boiling temperature in the presence of citric acid, whereby prior removal of sulfate appears to be unnecessary, and titrating in the presence of phenol red–bromothymol blue indicator instead of the customary phenolphthalein. According to Dubox (67) precipitation of the phosphomolybdate is facilitated under certain conditions by the ferric ion.

Other recently investigated volumetric methods adaptable to the analysis of fertilizers include titration of magnesium ammonium phosphate with standard acid in the presence of bromocresol green (275) or a bromophenol indicator (239); titration of an ammonium acetate–acetic acid buffered solution of the sample with zinc chloride (146); potentiometric titration involving the use of silver nitrate in the presence of alkaline buffers (80); precipitation of the phosphorus as bismuth phosphate and its subsequent determination by an iodometric procedure (94); and titration of a hydrochloric acid solution of the sample with sodium hydroxide in the presence of calcium chloride using a phenolphthalein–dimethyl yellow–methylene blue indicator (157). The use of ion-exchange resins for separating the orthophosphate ion from cations has been proposed (140, 141), and this principle is the basis of an accurate and rapid volumetric method developed by Helrich and Rieman (107) for determination of phosphorus in phosphate rock.

Thus far, little use has been made of colorimetric methods in the determination of phosphorus in fertilizers, owing chiefly to their generally very high degree of sensitivity and consequently to the large dilution factor involved in their application to such materials. Among several molybdenum-complex procedures that have been investigated recently (30, 34, 51, 139, 150, 180, 212, 268) the phosphovanadomolybdate method offers promise for rapid determination of phosphorus in phosphate rock (22). A spectrophotometric method of possible application to fertilizers is based on the change in light absorption by a ferric salicylate complex in the presence of phosphate ions (145). A photoelectric method involves titration of the phosphate with bismuth oxychlorate to maximum turbidity (46).

Fraps (87) outlines a procedure proposed by C. A. Butt for the determination of acid-soluble metaphosphate in phosphate supplements for animal feeding, which appears to be applicable to metaphosphate-containing fertilizers.

Laboratory methods of determining available phosphorus in fertilizers have continued to receive much attention. Assuming that the official neutral ammonium citrate method (14, p. 23) is satisfactory for evaluating ammoniated superphosphate mixtures of average phosphorus content, Ross and co-workers (101, 234) report results indicating that the method gives high values for available phosphorus in ammoniated mixtures of low phosphorus content and low values for those of high phosphorus content. Mechanical continuous agitation during the citrate digestion, as an alternative to manual intermittent shaking, was recently adopted by the Association of Official Agricultural Chemists (126, 128, 167). Allen (3) discusses certain factors and precautions in the preparation of neutral ammonium citrate solution.

Evaluation of fused tricalcium phosphate by means of the 2% citric acid method (14, p. 25) is proposed by MacIntire and co-

workers (166, 168). Other investigators (109, 127) point out, however, that the citric acid solubility of the phosphorus of this material, as well as that of other types of α-tricalcium phosphate products, is usually only slightly different from its solubility in neutral ammonium citrate. Although basic slag has long been evaluated by means of the 2% citric acid method, recent studies (109, 128) show that the neutral ammonium citrate procedure is also applicable to this material. Determination of available phosphorus in phosphate rock–magnesium silicate glass, a new type of fertilizer, involves problems that require further study (109, 112).

Margulis (175) proposes that the available phosphorus in superphosphates be determined by successively extracting the sample four times with water and titrating the extracts with sodium hydroxide. The results are said to agree well with those obtained by the ammonium citrate method. According to Meurice (183) adulteration of basic slag and bone meal with mineral phosphates can be detected with the aid of a 3% formic acid solution two-thirds neutralized with calcium carbonate.

POTASSIUM

In the United States the Lindo-Gladding (chloroplatinic acid) gravimetric method is the only official procedure for determining potassium in fertilizers (14, p. 31). Among recent studies of this method the proper concentration of alcohol for separating the potassium chloroplatinate has received major attention (3, 81, 83–86, 188, 248), with the final result that change of the alcohol concentration from 80 to 95% is recommended for official adoption (85). Recovery of the potassium is improved by saturating the alcohol with potassium chloroplatinate, especially when the alcohol concentration is lower than 90 to 95% (85, 248), as well as by precipitating and washing the chloroplatinate at temperatures below 30° C. (82, 83, 123). In agreement with previous workers, Mitchell and Ford (189) report that presence of phosphate causes low results for potassium. The customary ignition to destroy ammonium salts and organic matter preliminary to the chloroplatinate precipitation may result in loss of potassium. Joy (132) proposes a modification that avoids this possibility. Potassium can also be determined colorimetrically with the aid of chloroplatinic acid or iodoplatinic acid (1). Ford (83) outlines a procedure for recovery and purification of platinum from potassium determination.

The cobaltinitrite method for potassium is discussed by Tinsley (274) and others (38, 41, 59, 106, 137, 174). Cotte and Ducet (57) propose indirect determination of potassium by a procedure that involves reduction of the cobaltinitrite precipitate with ferrous and silver sulfates and estimation of the resulting ammonia. The zinc and magnesium cobaltinitrites are said to have advantages over the sodium salt as reagents for the qualitative detection of potassium (278).

Pyrolysis curves for several of the most used potassium precipitates have been determined (69).

Weaver and Lykken (286) describe a polarographic method for potassium, which is said to be applicable to a wide variety of materials. Procedures for determining potassium in fertilizers and other products, involving use of ion-exchange substances, are reported by Runneberg and Samuelson (241, 242, 244). Organic compounds that have been proposed as reagents for detection and determination of potassium include dipicrylamine (38, 144, 245), picrolonic acid (71), 5-nitrobarbituric acid (97), sodium 6-chloro-5-nitrotoluene-3-sulfonate (38), ethylenediaminotetraacetic acid (251), and 4,6-dinitrobenzofuroxan (220).

Use of the flame photometer method (27, 49), a rapid and accurate procedure for potassium in soils and plants (15, 195, 232), for analysis of potash ores is suggested by Barnes and co-workers (20). Application of this method in fertilizer analysis is worthy of study. Other rapid potassium methods, also based on physicochemical principles, are proposed for plant-control work in the

potash industry (142, 187). A method for analysis of sewage sludge involves calculation of the potassium from the amount of the chloride ion and the combined weights of potassium and sodium chlorides (225).

For determination of potassium in leucite Calcagni (40) favors decomposition of the sample with phosphoric acid. Other workers (100, 133, 177, 178) recommend mixtures of hydrofluoric and perchloric acids for decomposition of potassium silicates in general. Dilute acid, especially hydrochloric acid, is reported to be a better solvent than water for potassium in plant ash (56, 218).

CALCIUM

The classic method for calcium involves its precipitation as the oxalate and subsequent determination by gravimetric or volumetric procedures. The conditions for separation of calcium from magnesium in this manner have been further investigated by several workers (153, 161, 261, 295). Based on studies with a radioactive indicator Shvedov (261) reports that coprecipitation of magnesium with calcium oxalate increases in the temperature range 20° to 100° C. and is affected by the speed of neutralizing, rate of stirring, and other factors. He concludes that coprecipitation can be reduced to a minimum but never entirely prevented. For materials containing organic matter Stamberg and Bolin (265) recommend digestion of the sample with a mixture of perchloric and sulfuric acids in the presence of a little sodium molybdate.

Carvalho Ferreira (44) proposes novel volumetric procedures for direct determination of calcium which are based on the fact that in the presence of the oxalate ion ferric salts give no color with potassium ferrocyanide or thiocyanate. A new direct method for calcium in the presence of magnesium involves titration with sodium oxalate in the presence of cacotheline and ferrous iron (149, 281). Good results are obtained only when not more than twice as much magnesium as calcium is present (281). Titration of the oxalate with ammonium hexanitratocerate in the presence of Setopaline-C is recommended for small quantities of calcium (143). Scott and Johnson (252) report that, for a wide variety of materials, use of a spectrophotometer facilitates the determination of macro- and microquantities of calcium by the oxalate-permanganate procedure. Potentiometric titration of calcium with oxalate in the presence of chlorine, ammonium, and magnesium ions is possible (269). Use is made of the oxalate reaction in estimating the surface area of liming materials and other insoluble compounds (19).

Gravimetric determination of calcium as the normal molybdate has been proposed (124, 194). Although the method is said to be satisfactory for analysis of limestone, presence of magnesium in concentration greater than 0.1 N necessitates double precipitation of the calcium (194). For determination of calcium in the presence of large quantities of magnesium, precipitation as the tungstate is recommended by Peltier and Duval (204), who have also determined the pyrolysis curves for this and several other of the most used calcium precipitates (203) by means of the Chevenard thermobalance.

Recently proposed colorimetric methods for calcium are based on the use of chloranilic acid (21) or sodium tungstate and titanium trichloride (229). The latter method is applicable in the presence of a large excess of magnesium. Methods for potentiometric determination of calcium by precipitation as the fluoride—not applicable in presence of magnesium—involve titration with sodium fluoride in the presence of ethanol and ferrous and (or) ferric chlorides (269, 279).

MAGNESIUM

As with phosphorus, precipitation as magnesium ammonium phosphate and conversion to the pyrophosphate for weighing have served long and well as a principal method for magnesium. Re-

cent studies of several factors involved therein are summarized in the section on phosphorus (68, 129, 153, 164, 171, 250, 277). Contamination with manganese is avoided by precipitating the phosphate in the presence of an alkali cyanide (275). Acidimetric titration of magnesium ammonium phosphate has been further investigated, with special reference to choice of indicator (239, 264, 275). The best results are obtained with methyl orange or neutral red–bromocresol green mixture; the latter gives the sharpest and most easily discernible change (264).

Determination of magnesium by means of 8-hydroxyquinoline has been studied by several workers (43, 66, 92, 176, 262, 267). The procedures include polarographic methods (43, 267) and a colorimetric semimicromethod (66), the latter said to be applicable to samples containing considerable calcium and phosphate.

A new procedure for magnesium involves its precipitation as magnesium ammonium arsenate hexahydrate and iodometric determination of the arsenic (182). Pyrolysis curves for several of the most used magnesium precipitates have been determined (68). For quantitative separation of magnesium in a dense coarsely crystalline form and its subsequent determination by permanganate titration, Gordon and Caley (95) recommend precipitation with pure diethyl oxalate in 85% acetic acid solution. The method is applicable to calcium-free solutions. According to Sacconi (243), 1,3-bis[3-methyl-4-nitro-5-pyrazolyl]-triazene is a specific reagent for magnesium.

In recently proposed methods for rapid determination of magnesium in magnesite, dolomite, and similar materials, the acid solution of the sample is neutralized with calcium carbonate and titrated with alkali (32, 52). The titration is made either at the boiling temperature using an alcoholic solution of trinitrobenzene as indicator (52) or potentiometrically in hot 50% ethanol with thymolphthalein as an aid in locating the end point (32). The accuracy of the latter procedure, which is applicable in the presence of elements commonly associated with magnesite and dolomite, is said to be comparable to that of the gravimetric phosphate method.

Although considerable attention has been given to laboratory methods of evaluating water-insoluble magnesium in fertilizer materials and mixtures (103, 151, 219, 254, 263, 264, 289), especially with reference to solubility in ammonium citrate solutions, no official procedure for this determination has yet been adopted.

SULFUR

Recent investigations of the gravimetric barium sulfate method include studies of its solubility in the presence of excess chloride or sulfate ion (122), formation of insoluble complexes with phosphate (209), and other factors (104, 105).

Volumetric procedures based on precipitation of the sulfate as the barium salt include titration to maximum turbidity with the aid of a photometer (applicable in the presence of phosphate, 46, 47); a conductometric method which is accurate in the presence of large amounts of chloride but is subject to interference by calcium (7); titration with barium chloride using tetrahydroxyquinone (200) or dipotassium rhodizonate (2) as an indicator; and conversion of barium sulfate to the carbonate, with acidimetric titration of the latter (73).

Leclerc (154) determines sulfur by precipitation as lead sulfate and titration of the excess lead with ammonium molybdate in the presence of sodium alizarin sulfonate. Formation of lead sulfate and its characterization by means of sodium rhodizonate are the basis of a spot test for calcium sulfate in fertilizers (79).

BORON

The official methods for boron in fertilizer materials and mixtures (14, pp. 32–4) employ the well-known titration of boric acid with sodium hydroxide in the presence of mannitol. Hollander

and Rieman (*118*) state that with a large excess of mannitol over boric acid the titration error is small and the end point is sharp at a concentration of about 0.35 mole of mannitol per liter of solution at the potentiometrically determined equivalence point. The optimum mannitol–boric acid ratio depends on the initial volume of the solution. Ruehle and Shock (*240*) use the mannitol titration precedure in potentiometric determination of small quantities of boron by a null-point method.

Improvements in the quinalizarin colorimetric method for boron include the use of a combination quinalizarin–sulfuric acid solution and special equipment for storing and dispensing the reagent (*26*). Evans and McHargue (*77*) recommend substitution of carmine for the quinalizarin. For analysis of fertilizers and plant ash, Stettbacher (*266*) proposes a colorimetric method using a concentrated sulfuric acid solution of chromotrope-B (*p*-nitrobenzenazo-1,8-dihydroxynaphthalene-3,6-disulfonic acid) with prior distillation of the boron as the trimethyl ester if necessary. Austin and McHargue (*16*) report interference in the chromotrope reaction by the nitrate, nitrite, and fluorine ions, but little or no interference by 28 cations. Philipson (*207*) employs the turmeric reaction in a colorimetric micromethod for boron. Monnier and co-workers(*191,192*)describe a procedure for borax which involves conversion of the boron into the colorless stable complex BF_4^- and photometric determination of the excess fluoride ion with the aid of a mixture of ferric chloride and sulfo-5-salicylic acid.

MANGANESE

The two official methods for manganese in fertilizers (*14*, p. 36) —the colorimetric permanganate and the volumetric bismuthate procedures—were adopted after extensive collaborative studies by Smith and Deszyck (*263*). In the persulfate method as modified by Hillson (*114*), addition of disodium phosphate to the solution facilitates reduction of excess persulfate, and use of osmium tetroxide as a catalyst aids in the arsenite titration of the permanganate.

A new method for manganese is based on potentiometric titration of manganous ion with permanganate ion in sodium pyrophosphate solution (*91, 162, 285*). According to Krause (*147*) manganese can be determined by titration with diammonium phosphate in boiling ammonium acetate–acetic acid buffered solution. Kvalheim (*152*) outlines a spectrochemical method for manganese, potassium, calcium, magnesium, and other elements in minerals, rocks, slags, and related substances.

COPPER, ZINC, AND COBALT

The iodometric method for copper and the gravimetric zinc oxide and the colorimetric dithizone methods for zinc in fertilizers (*14*, pp. 37-9) have been studied in much detail by Gary (*89*). Holmes (*119*) outlines dithizone methods for copper and zinc in soils, which are also applicable to fertilizers. Eisenberg and Keenan (*72*) describe a chemical microscopic test for the identification and differentiation of copper and zinc by means of their crystalline picrolonates.

Krause (*146*) proposes titration of the zinc ion with diammonium phosphate in boiling ammonium acetate–acetic acid buffered solution. The method fails in the presence of calcium, strontium, barium, and certain other ions. A new colorimetric method for zinc makes use of chloranilic acid (*21*).

A method for cobalt (*119*) involves its separation by means of dithizone and spectrophotometric determination as the nitrocresol compound. Prolonged heating and evaporation in determining cobalt as potassium cobaltinitrite may result in explosions (*37, 96*).

MOLYBDENUM

Molybdenum is reported to be essential for the growth of certain crops but the plant's requirement is extremely small and soil deficiencies in this element are known in only a few parts of the world. Although molybdenum *is at present of very minor concern* to the fertilizer analyst, its determination is of interest because of its widespread occurrence in trace quantities in phosphate rock and superphosphate (*117, 198, 231*). For the analysis of such materials Robinson (*231*) fuses the sample with sodium carbonate and determines molybdenum in the silica-free extract by means of the well-known thiocyanate colorimetric method. He also outlines a procedure for determination of rare earths in the residue from the molybdenum extraction.

CHLORINE

The fertilizer analyst is interested in determining chlorine because of limitations on the quantity of this element permitted in certain fertilizers, particularly those for tobacco. Recent study (*160*) of the time-honored Mohr procedure, which is the official method for chlorine in fertilizers (*14*, p. 34), leads to the conclusion that the titration is accurate in acidic solutions down to pH 4 if a correction is applied for the indicator blank. For solutions that are acid to methyl red, titration at pH 4.7 in the presence of a sodium acetate–acetic acid buffer is recommended.

Potentiometric titration of the chloride ion with silver nitrate has been investigated by several workers (*63, 64, 190, 297, 298*). The method proposed by Dean and Hawley (*63*) eliminates the use of a salt bridge, and avoids interference by a number of the ions commonly present in fertilizer solutions.

FLUORINE

Although fluorine is not known to be an essential plant-nutrient element, methods for its determination are of much importance to the fertilizer chemist because of its universal occurrence in mineral calcium phosphates and most phosphatic fertilizers and its relation to the processing and utilization of such materials. Methods for separating and determining fluorine are critically reviewed by Rinck (*228*). The methods commonly used for this element in fertilizers are based on distillation of the sample with perchloric acid and titrimetric determination of the recovered fluorine with the aid of thorium nitrate and sodium alizarin sulfonate according to the procedure originally proposed by Willard and Winter (*293*) and further developed by other workers (*60, 61, 90, 121, 221-224*). Apparatus for steam distillation of the fluorine in a multiple-unit arrangement, first proposed some years ago (*224*), has been improved (*50, 292*).

Titration with thorium nitrate in the presence of Solochrome Brilliant Blue B.S. is recommended for very small quantities of fluorine (*186*). Other recently described methods for fluorine include titration with aluminum chloride, using Eriochromcyanine R as an indicator (*247*); and colorimetric determination by means of ferric chloride and 5-sulfosalicylic acid (*191*) or with the aid of titanium trichloride (*193*).

CARBON DIOXIDE

For determination of carbon dioxide, Erickson and co-workers (*75*) favor decomposition of the sample with trichloroacetic acid, while Shaw and MacIntire (*257*) suggest the use of perchloric acid. Ingleson and Bentley (*125*) recommend absorption of the carbon dioxide in barium hydroxide under reduced pressure and titration against thymol blue, instead of phenolphthalein, but Pieters (*210*) prefers cresolphthalein. Speed and precision are said to be the chief advantages of the steam-distillation procedure developed by Shaw and MacIntire (*257*). A method and apparatus for direct measurement of the carbon dioxide evolved from acid-treated samples are described by Fahey (*78*). Other developments in apparatus for determination of this compound include a new type of alkalimeter (*31*) and a combined absorption and titration tube (*230*).

ACID- OR BASE-FORMING QUALITY

The method for determination of the acid- or base-forming quality of fertilizers (*14*, p. 40) is based on the procedure proposed by Pierre (*208*) about 15 years ago. The method which involves igniting the samples with sodium carbonate and sucrose or carbon black, digesting with hydrochloric acid, and titrating with alkali. has been studied in considerable detail by Allen and Gault (*5*) who have developed a number of improvements therein.

NEUTRALIZATION VALUE

In recent years increasingly large quantities of calcium silicate slags from iron blast furnaces and phosphate rock reduction furnaces (*169, 170*) have been used as soil liming agents. Determination of the neutralization value of such slags (*14*, p 44) presents problems of titration and of correction for sulfides as well as other complications, which have been investigated by Schollenberger (*249*) and especially by Shaw (*255, 256*). The latter concludes (*256*) that for blast furnace slags satisfactory results are obtained by titrating to pH 5.2 as indicated by cresol green, and allowing a calcium carbonate equivalence of 3.5% for sulfides

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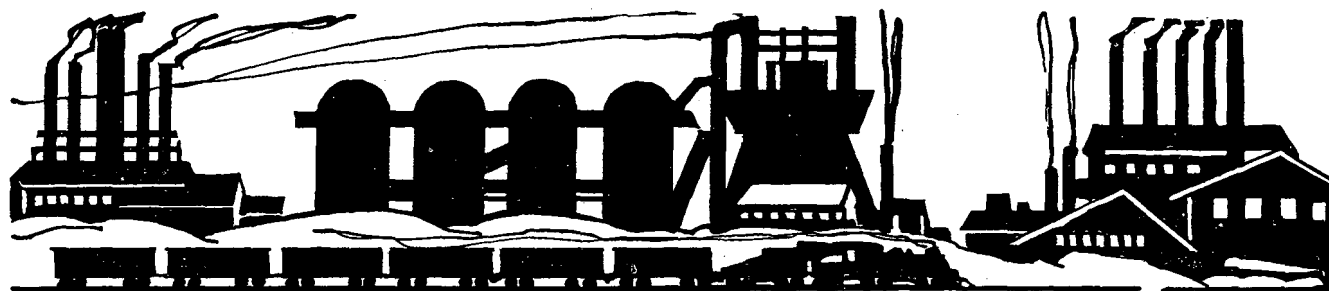
FOOD

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THE ultimate objectives of the food analyst and the variety of techniques employed to achieve them make this branch of chemistry particularly fascinating. The analytical methods of the food chemist may be applied in the development and enforcement of standards of identity, purity, or value; in problems of decomposition or spoilage under either normal or abnormal storage conditions; in studies designed to improve or control the quality of natural or processed foods; or in the determination of the nutritive value of foods for scientific, dietary, or labeling purposes. Interest in many of these objectives stems directly or indirectly from our federal and state food laws which are probably more comprehensive and more stringent than those of any other country in the world.

The major advances in food analysis during the past five years have resulted principally from the application of spectrophotometric, chromatographic, and microbiological technology. In this respect food chemistry, like the entire field of biochemistry of which it is a part, has encroached upon the provinces of bacteriology and physics and has made important contributions to both of these sister sciences.

A large share of the newer developments in analytical techniques have been concerned with the determination of the micronutrients—i.e., vitamins, trace minerals, and amino acids, the latter included here only by reason of the similarity in analytical methodology.

Because of the wide scope of procedures involved in food analysis it is hardly possible to discuss all phases critically in the limited space available. Moreover, to do so would require a range of experience beyond that to which the writer can justly lay claim.

MOISTURE

The wartime need for dehydrated foods stimulated the search for more rapid and accurate methods for determining moisture. The Karl Fischer reagent has proved to be most adaptable for this purpose. Reports have described application of the procedure to cereals, starches, vegetables, egg powder, soup mixes, and oils (*42, 127, 195, 224, 291, 330*). Moisture determinations can be completed in less than 2 hours. The method is applicable to products for which oven-drying methods are known to be inaccurate. For reliable results, however, it is essential that the reagent be standardized frequently. Substances which have high iodine absorption capacities—e.g., ascorbic acid—may interfere. An adaptation of the Karl Fischer method for sugar solutions entails the use of a specially designed flask for conducting the titrations in a closed system (*391*).

Vapor pressure measurements have been adapted to the study of the moisture content of dehydrated vegetables (*121, 236*). A more recent method involves the use of lyophilization—i.e., freeze-drying in vacuum in the presence of a water absorbent (*237*). This method has the advantage of not requiring precise control of drying temperature, as the final dry weight is practically independent of the temperature.

CARBOHYDRATES

Numerous papers have appeared on the determination of monosaccharides and disaccharides in mixtures. It has been shown (*191*) that the use of the citrate-carbonate copper reagent for the analysis of dextrose, levulose, invert sugar, and sucrose-invert sugar mixtures is less precise than the Munson-Walker or Lane-Eynon methods. However, it is satisfactory for rapid or occasional work where a precision of less than 0.5% will suffice. A combination of copper-reducing methods applied before and after fermentation has been employed in the determination of dextrose and levulose in cane products containing unfermentable reducing substances (*392*). Equations relating titer to concentration in the Lane-Eynon method or in the direct determination with alkaline ferricyanide yield results in close agreement with those given in the Lane-Eynon tables (*393*). The Kiliani reaction has been adapted to the direct determination of reducing groups in sugars, the cyanide reacting mole for mole with aldehyde, ketone, hemiacetal, or hemiketal (*247*). Several papers have appeared on the adaptation of Bial's orcinol reagent to the estimation of pentoses and pentosans (*44, 233, 246*).

A polarimetric method for the determination of maltose in the presence of glucose is based upon the addition of sodium bisulfite, which eliminates the optical rotation of the former but affects the rotation of maltose and dextrins only slightly (*46*). It has been suggested that the molybdenum blue reaction for glucose in the presence of sucrose may be applicable to the determination of any reducing monosaccharide in the presence of disaccharide (*27*). Good agreement with the Munson-Walker method is reported by this procedure. Roe's resorcinol procedure has been applied to the determination of fructosan in plant materials (*234*); methods are described for correcting for the interference of starch when present in excessive proportion. Of some interest to food chemists are recent methods described for the identification of glucose (*163*), fructose (*269*), and methylpentoses (*97*). The determination of aconitic acid in sugar house products and in mixtures with citric acid has recently been reported (*7*). A method for caramel in wines, distilled spirits, vinegar, and vanilla extract (*233*), which is based upon Lovibond tintometer readings of extracts, would appear to be improved if adapted to photometric measurement.

Several procedures have been adapted for the determination of starch in plant materials. One of these (*346*), recommended for samples containing at least 10% starch, entails quantitative precipitation of the starch via starch iodide, removal of protein with uranyl acetate, and determination of the optical rotation. Another (*293*) consists in extraction of the dried plant tissue with perchloric acid, quantitative precipitation as starch iodide, decomposition of this complex, acid hydrolysis of the starch, and estimation of the glucose by Somogyi's volumetric procedure. This method requires not more than 250 mg. of sample. It is claimed to have a precision of ±2% and to be independent of the relative proportions of amylose and amylopectin comprising the starch.

Increased interest in uses for pectin is reflected in improved methods for the determination and evaluation of this substance. A method has been adapted for the determination of pectin in biological materials based on its conversion to pentose and subsequently to furfural which is determined colorimetrically (*47*). The sources of error in the Zeisel method for determination of the methoxyl content of pectin have been investigated (*193*) and improved procedures have been proposed (*165*). The preferred method utilizes the enzyme pectase for hydrolyzing pectin methyl ester and corrects for methyl ester remaining unhydrolyzed. Where the specific type of pectin is known, more rapid saponification procedures can be used requiring no special apparatus, as does the Zeisel method. A novel electrolytic procedure has been described for the determination of pectin or pectic acid in solutions after de-ashing by means of ion exchange resins (*377*).

PROTEINS AND AMINO ACIDS

Some of the factors affecting the completeness of digestion in the modified Kjeldahl methods for the determination of nitrogen have been discussed (204, 249). It has been shown that fractionation of protein concentrates for intact (copper-precipitatable) protein, protein decomposition products (precipitatable by phosphotungstic acid), undigestible protein, and hot water-soluble protein yields data that can be correlated with the nutritive value of such concentrates for chicks (6). The baking quality of nonfat dried milk solids in bread is said to be roughly predictable from the protein content of the whey as determined by a rapid turbidimetric method (156).

Among the many papers on the nutritional evaluation of proteins in food products based on correlating their chemical composition with animal tests, two reviews are worthy of note (241, 253). A discussion of the importance of the level of protein intake upon the growth response of rats (20) suggests that the maximal utilization of absorbed protein is the most valid criterion for assessing its growth-promoting quality. Prediction of nutritive value from amino acid composition has been attempted by comparing the percentage deviation of the content of each essential amino acid from the corresponding composition of a completely digestible and utilizable reference protein—i.e., whole egg protein (254). Limitations in this procedure are discussed, particularly as applied to proteins whose nutritive value may be either augmented or diminished by heat treatment without demonstrable change in their amino acid composition.

The problem of effecting acid hydrolysis of protein in the presence of carbohydrates without loss of certain of the amino acids continues to beset workers in this field. A procedure adapted for fresh vegetables (2) entails the treatment of the acetone-extracted residue with hot 90% formic acid and precipitation of carbohydrates with ethanol, the filtrate containing almost all the nitrogen of the fresh product. In the form described, however, this technique is not adapted to other foodstuffs, possibly because of variations in carbohydrate-protein relationships, particle size, and other physical characteristics.

Chemical Methods for Amino Acids. The most rapid progress in the analysis of proteins for individual amino acids has been achieved by microbiological methods, although substantial advances have been reported in the chemical determination of certain of the amino acids. An improved adaptation of the Sakaguchi reaction for arginine is based on the greater stability and intensity of color when 0.06 N sodium hypochlorite is substituted for a stronger hypobromite reagent (3). Modifications of the Kapeller-Adler reaction for phenylalanine are reported which correct for the interference of tryptophan (45) and other amino acids (161). The latter procedure, which is said to be capable of detecting 6 micrograms of phenylalanine per ml., involves the nitration of phenylalanine, reduction to diaminophenylalanine, and coupling in slightly acid solution with 1,2-naphthoquinone-4-sodium sulfonate to yield a red compound. A procedure for determining tryptophan, phenylalanine, and methionine on the same alkaline hydrolyzate of protein has been described (162). The colorimetric estimation of tryptophan by reacting with p-dimethylaminobenzaldehyde has been improved and adapted for meals and flours. It involves preliminary papain digestion which hydrolyzes the nitrogenous material, leaving the starch and fiber in suspension (175). The ultraviolet absorption spectra of tyrosine and tryptophan in alkaline solution provide the basis for their determination in mixtures where the molar ratios are not greater than 20 to 1 either way (142). Correction must be made for continuous irrelevant absorption in proteinaceous materials. A spectrophotometric adaptation of the glyoxylic acid reaction for tryptophan requires preliminary separation from tyrosine and phenylalanine (60).

Spectrophotometric adaptations of the Sullivan reaction for cysteine (88, 117) are claimed to give better conformity to Beer's law. In these methods the cystine is separated from the hydrolyzate in the form of cuprous mercaptide and the color resulting from the reaction with sodium 1,2-naphthoquinone-4-sulfonate in alkaline bisulfite medium is read promptly. The difference in susceptibility of cystine and methionine to oxidation is used as a basis for their determinations in plant and animal products (116). The alkaline nitroprusside reaction has been adapted to the colorimetric estimation of methionine (176). By a modification of the method of Nicolet and Shinn for serine and threonine, good agreement is shown between the estimations based on the aldehyde and the ammonia formed in the periodate reaction (308). A colorimetric method for isoleucine, based on its degradative oxidation to ethyl methyl ketone, appears to be reproducible, although the results are somewhat higher than those obtained by the microbiological or other chemical procedures (4). A method for glutamic acid in proteins is based upon the loss in amino nitrogen resulting from its transformation to pyrrolidonecarboxylic acid; a correction is required for the interference of cystine (276). A biochemical method which appears to have high specificity for l(+)-glutamic acid involves decarboxylation by means of an enzyme extracted from squash; the liberated carbon dioxide is measured manometrically (324).

Thus, despite the great advances being made in the microbiological estimation of amino acids, efforts to improve the specificity and sensitivity of chemical procedures are by no means at a standstill. The possibilities of the newer types of instrumentation are also being explored in this field. Polarographic studies have been reported on the acid-insoluble fraction from iodoproteins (337) and on amino acids (203), the latter by means of reduction of their copper complexes.

Chromatography. One of the most useful analytical tools developed during the period covered by this review is chromatography, especially its adaptation to paper strips and sheets, for which the English workers are largely responsible. In a classical paper published in 1944, Consden, Gordon, and Martin (79) described the use of moisture-saturated paper as the stationary phase and various solvents as the mobile phase in the qualitative analysis of protein hydrolyzates. By first effecting chromatographic separation in one direction, then drying and running another solvent at right angles, two-dimensional separation of the 20-odd amino acids in protein hydrolyzate can be achieved. The position of the individual amino acids, as identified by known controls, is revealed by the blue areas which appear upon spraying with ninhydrin solution and heating. After identification of the loci of the zones, the adsorbed compounds may be eluted from companion strips or sheets and determined quantitatively by microbiological procedures (81).

In addition to the amino acids, partition chromatography has been applied to the analysis of various complex biological mixtures of vitamins, sugars, organic acids, and antibiotics. This relatively simple means of effecting the separation of chemically similar substances, when combined with microchemical or microbiological analytical procedures, opens new vistas for the analytical chemist.

Several reports have appeared on the use of silica gel in the chromatographic separation of acetamino acids (143) and monoamino acids (360). A theoretical study has been reported on the separation by silica jelly ionophoresis of substances of different ionic mobility, such as amino acids and peptides (80). A procedure has been described for the chromatographic separation of the individual basic amino acids from mixtures by fractional elution of a single adsorption on a mixture of Lloyd's reagent and Hyflo Super-Cel (30). Arginine, histidine, and lysine were determined in the eluate by modifications of the Sakaguchi, Pauly, and ninhydrin reactions. Several investigators have reported the use of synthetic anion exchange resins, such as Amberlite IR4, for the separation of the dicarboxylic amino acids (58, 76, 82, 354). Quantitative chromatographic separation of phenylalanine, leucine, isoleucine, methionine, tyrosine, and valine have been

effected on a column packed with potato starch (345). An automatic device is used in the fractional elution of a large number of small effluent fractions which are then analyzed microbiologically.

Chromatographic techniques have entered into most of the recent work on the distribution of carotenoids in plant tissue. Methods have been described for the determination of the vitamin A-active pigment, carotene, itself (63, 147, 301, 373) in alfalfa and similar grasses, and together with preformed vitamin A in mixed feeds (86, 265). By the appropriate choice of the developing solvent it has been found possible to separate β-carotene from certain of its stereoisomers (31). Chromatographic procedures have also been described for the separation of free vitamin A from its esters (138, 307). Partition chromatography has been applied to the separation and determination of the straight-chain, saturated fatty acids of chain lengths ranging from C^1 all the way to C_{18} (113, 122, 159, 287, 302, 303, 305, 306).

The separation of the sugars has likewise been affected by this means. Paper chromatography has been used in qualitative analysis of reducing sugars in such varied materials as apple juice, egg white, and blood (62, 283). Ammoniacal silver nitrate is employed to identify the position of reducing sugars on the strip, although later work suggests that the fluorescence produced by condensation of the reducing sugars with m-phenylenediamine yields less equivocal results. Both silica gel (189) and filter paper (126) have been used in the chromatographic separation of the organic acids in fruit. This principle has been applied in the determination of lactic and succinic acids in milk and egg products, respectively (74). Of special interest to the biochemist has been the application of paper chromatography to the isolation of purines, pyrimidines, and nucleosides from hydrolyzates of nucleic acid (184).

Measurements of the characteristic ultraviolet absorption spectrum or of the color produced with antimony trichloride form the basis for improved methods for the physical-chemical estimation of vitamin D in fish liver oils or in products of the irradiation of ergosterol, after removal of interfering impurities by chromatography (95, 120). The use of chromatography as an analytical and research tool is being thoroughly and successfully explored. In the writer's opinion, this is only the beginning of what can be realized in the solution of many vexing problems of separating closely related compounds.

Microbiological Assays for Amino Acids. Substantial advances have been made during the past five years in revising and improving methods of microbiological assay for amino acids (for recent reviews see 102, 332, 340). Several systems of assay are based on the use of a single organism for a number of different amino acids. For example, a system of assay is described (150, 349) for nine essential amino acids using Streptococcus faecalis as the test organism; the tenth, phenylalanine, is determined with Leuconostoc delbrückii. More recently a procedure for 13 amino acids has been reported based on the use of Clostridium perfringens (Welchii) (39) which is claimed to have the advantage of not requiring aseptic conditions. The tendency, however, seems to be to prefer methods requiring more than one organism for the series of amino acids, each designed to take advantage of the greater accuracy resulting from the specific requirements of the microorganism, special adaptations of media, conditions of incubation, etc. Aside from the conditions affecting bacterial growth, the principal technical difficulties are concerned with the preliminary preparation of the protein hydrolyzates without destruction or racemization to inactive forms. Attempts have been made to overcome the difficulties of acid hydrolysis of foods (destruction of amino acids, formation of inhibitors) by modifying the conditions of hydrolysis, by the use of alkaline hydrolysis, or by adaptation to direct determination on unhydrolyzed material.

A wide variety of organisms is employed in these basically similar microbiological determinations. The following recent papers illustrate the use of one or more organisms for each amino acid: arginine, L. casei (231) and Streptococcus faecalis (182): histidine, Leuconostoc mesenteroides P-60 (105, 106, 181), Lactobacillus fermenti 36 (108), and Streptococcus faecalis (181); lysine, Leuconostoc mesenteroides (104, 178); tryptophan, Lactobacillus arabinosus (144, 145, 389), Eberthella typhosa (389), and Tetrahymena geleii (312); phenylalanine, Leuconostoc mesenteroides and Lactobacillus casei (107); methionine, Lactobacillus fermenti (103), Leuconostoc mesenteroides (226, 228, 310) Lactobacillus arabinosus (177), and Streptococcus faecalis (228, 349); threonine, Lactobacillus fermenti (109) and Streptococcus faecalis (179); leucine, Lactobacillus arabinosus (55, 331) and leucineless Neurospora crassa (173); valine, Lactobacillus casei (231) and Streptococcus faecalis (180). In addition to these microbiological methods for the essential amino acids, there are the uniform assay procedures cited above in which a single organism is used for a large number of essential amino acid determinations. Several papers have described Lactobacillus arabinosus assays for glutamic acid (152, 223, 227). Leuconostoc mesenteroides has been employed in the assay for aspartic acid (151). Microorganisms play a somewhat different role in another method for l-aspartic acid; here the enzyme aspartase, extracted from a dry preparation of Pseudomonas fluorescens, catalyzes the hydrolysis to fumaric acid and ammonia, the latter serving as an index for the estimation of this amino acid in casein hydrolyzate (364).

Analytical data for the amino acid content of proteins and of foods are given in many of the papers cited above as well as elsewhere (23, 160, 164). Henderson and co-workers (160) describe a micromethod for microbiological determination of amino acids adaptable to as little as 0.2 ml. of sample. They also describe an apparatus for titrating electrometrically directly in the culture tube and a mechanical device for automatically dispensing desired volumes or sequence of volumes from 0.02 to 0.1 ml. with an accuracy of ±1%. A simple device for titrating the contents of culture tubes electrometrically to a desired end point has been described for larger volumes of solution (232).

The use of microbiological methods has been extended to the determination of not only amino acids and vitamins (see below) but also cytosine, uracil, and thymine (244) and, strangely enough, to the determination of trace quantities of manganese (29) which is required by Lactobacillus arabinosus. The requirement of Streptococcus faecalis R for potassium is the basis for a microbiological assay for that element (21). Several lactic acid bacteria require oleic acid, which suggests the possibility of microbiological assays for fatty acids (380).

In methods for designing and calculating microbiological assays the slope-ratio procedure is proposed in preference to interpolation from standard dose-response curves (387, 388).

<center>VITAMINS</center>

Chemical and Physical Methods. The methods employed in the determination of carotene in plant tissue involve extraction or phasic separation, chromatographic adsorption, and colorimetric or spectrophotometric measurements of the eluates or filtrates. In the isolation and extraction step it is essential to avoid conditions that permit isomerization. The tendency seems to be away from phase separation methods because they are not always quantitative and specific for the biologically active carotenes. The removal of chlorophyll from plant tissues can be effected by means of a variety of adsorbents including barium hydroxide, calcium carbonate, soda ash, hydrated lime, dicalcium phosphate, or fat-free bone meal.

An illustrative method for the determination of carotene in dehydrated alfalfa involves extraction of the finely ground, dried leaf by allowing it to stand in the dark overnight in a mixture of

1 part of acetone and 2 parts of Skellysolve B, thus tending to avoid oxidation and isomerization due to heating (*336, 369*). [A more recent paper (*255*) suggests the use of preliminary blanching to avoid oxidation loss during the drying of alfalfa and cereal grasses.] The extract is concentrated and chromatographed on a column of 2 parts of Hyflo Super-Cel and 1 part of magnesia. Elution is effected by means of 4% acetone–Skellysolve B, and β-carotene and neo-β-carotene-D are estimated with a Beckman spectrophotometer. In a method adapted to the determination of β-carotene in sweet potatoes and products, isomerization is claimed to be avoided by extraction with ethyl alcohol (*275*). This paper contains an extensive discussion of the effect of the solvent on the spectrophotometric characteristics of the carotenes. Iso-octane is recommended because of its ease of purification.

The analyst is often confronted with the determination of both carotene and preformed vitamin A in the same food or feed. Ultraviolet spectrophotometry and the Carr-Price reaction are the principal nonbiological procedures employed for vitamin A measurement. The former is widely used in the evaluation of fish liver oils and their products, in which relatively little irrelevant absorption is present. Vitamin A absorption curves can often be "cleaned up" by removing the saponifiable impurities. The validity of $E_{1\ cm}^{1\%}$ at the peak of absorption (325 to 328 mμ), as an index of vitamin A content is dependent on the conformity of the shape of the observed curve to that of true vitamin A. Experience has justified the more or less arbitrary limit of 0.72 for $E_{300/328}$ adopted during the war (*280, 282*). In a study of spectrophotometric changes occurring during the oxidation of vitamin A oils (*155*) the ratio $E_{280/328}$ has been shown to increase over a relatively wider range during oxidation than $E_{300/328}$ and hence to be a more sensitive index of oxidation. (The absorption minimum for pure vitamin A in this region is 260 mμ.) However, in commercial liver oils irrelevant absorption is likely to be greater at the lower wave lengths than at 300 mμ.

The most important recent contribution to the spectrophotometry of vitamin A has been a mathematical method for correcting absorption curves for the extent of their deviation from that of true vitamin A (*259–261*). From extinction measurements made at wave lengths slightly below and above the absorption maximum for vitamin A, corrections can be made for distortion of the shape of the curve and displacement of its height by irrelevant substances. This principle can be applied generally in spectrophotometric analysis, provided the basic assumption holds true—viz., that irrelevant substances absorb linearly within a narrow range on each side of the peak. A nomogram has been described to facilitate the use of the Morton-Stubbs correction in vitamin A determinations (*278*). This procedure is proving useful in the estimation of vitamin A in fish liver oils and it appears likely that vitamin A might be determined in this manner in the unsaponifiable extract of foods.

By means of a modified flowing cell apparatus studies have been made of the kinetics of the antimony trichloride reaction for vitamin A (*53, 135*) as applied to vitamin A alcohols, esters, and the common carotenoid pigments. The fact that the colors produced by these substances increase, decrease, or remain stable with time, the rates being influenced by light, provides the basis for their estimation when present together. These principles have been applied in the determination of vitamin A in mixed feeds (*41*). A special cuvet holder has been devised for conducting the antimony trichloride reaction in a Beckman spectrophotometer. It is claimed that readings can be made in this instrument within an average time of 7 seconds (*201*). In the direct-reading Evelyn photometer it has been observed that the maximum occurs within 4 seconds but the rate of fading is dependent upon the intensity of the incident light. Hence it may be possible to use a null point instrument, provided the light source is of sufficiently low intensity. The need for accurate

calibration of photometers in antimony trichloride estimation of vitamin A has been stressed (*54*).

Activated glycerol dichlorohydrin produces a fairly stable violet color with vitamin A (absorption maximum 555 mμ). This reagent has been found to give results with fish liver oils in substantial agreement with the antimony trichloride method (*343*). It has been reported that poultry mashes contain substances which suppress the reaction but which can be removed by adsorption on a mixture of Hyflo Super-Cel and activated magnesia (*368*). Because this procedure also removed vitamin A alcohol, it is applicable when the poultry mashes contain vitamin A only in the form of ester.

As indicated above, the nonbiological evaluation of foods for vitamin A becomes more complicated when preformed vitamin and carotenoids are both present. In a spectrophotometric method for the estimation of preformed vitamin A in dehydrated eggs, correction is made for the presence of the carotenoid pigments characteristic of this food (*329*). The correction allows for the effect of isomerization in the heating and extraction procedure and is made by subtracting 15% of the optical density at 450 mμ from the optical density at 326 mμ. The spectrophotometric method for the determination of carotenoids in dehydrated egg powder has been combined with a method for the fluorometric determination of the brown, ether-soluble lipide amine-aldehyde pigments whose presence is correlated with loss of palatability on storage (*36, 110*).

Studies on the spectrophotometric and colorimetric estimations of vitamin A and carotenoids in butterfat (*141, 394, 395*) indicate that accurate correction cannot be made for the interference of carotenoids at the absorption maximum corresponding to preformed vitamin A. Correction for the blue color resulting from carotene involves certain arbitrary assumptions and errors—for example, failure to take account of isomerization and differences in the biological activity among the carotenoid pigments. However, it would appear to have practical utility. The Carr-Price reaction has been applied to the determination of vitamin A and carotene in milk (*40, 168*). Studies on the effect of azo dyes upon the colorimetric estimation of vitamin A in butterfat (*395*) are pertinent to the assay of colored margarine.

The estimation of preformed vitamin A in margarine has not, thus far at least, been complicated by the presence of added carotene. To avoid or correct for irrelevant absorption, spectrophotometric methods (*38, 225, 266, 281, 309, 374*) employ an adsorption and elution step as well as the photolytic destruction of vitamin A. However, the conclusion reached in a series of collaborative studies under the auspices of the National Association of Margarine Manufacturers (*309*) was that the antimony trichloride procedure is better suited than direct spectrophotometry for margarine assays, especially when unfortified control samples for each type of margarine are unavailable. It is important that the spectrophotometric estimation of vitamin A in margarine be re-examined in the light of the Morton-Stubbs correction for irrelevant absorption (*261*).

Colored products of the reaction of antimony trichloride with vitamin D and their provitamins have been applied to their estimation in fish liver oils and concentrates, and to the products of the irradiation of sterols (*95, 119, 219*). These methods are limited by the fact that vitamin A and other sterols present in natural materials interfere. However, in the case of high-potency fish liver oils, chromatography may be employed to separate the vitamin D fraction (*95*). A recent improvement (*56*) has been reported in the sensitivity of the glycerol dichlorohydrin reaction for vitamin D$_3$ (*342*), but further work is necessary to adapt this method to the estimation of vitamin D in oils containing less than 100,000 units per gram.

Chemical methods for the estimation of the tocopherols depend largely on the earlier procedures of Emmerie and Engel and of Furter and Meyer. An improved degree of specificity is claimed

for a modification of the latter procedure (68) involving chromatographic separation of the red o-quinone obtained after nitric acid oxidation of the unsaponifiable extract. However, this method does not distinguish between the tocopherol isomers. Most investigators appear to prefer modifications of the Emmerie-Engel method. A critical comparison with the Furter-Meyer procedure, as applied to plant extracts, has been reported (370). Careful precautions are necessary against oxidation during the saponification step and for removal of carotenoids which, like tocopherols, react with the ferric chloride–α,α-dipyridine reagent. The use of special apparatus (68) or of pyrrogallol (358) to prevent oxidation during saponification has been described; for the removal of interfering carotenoids, sterols, etc., adsorption of floridin is recommended (68, 207, 358). A microadaptation of the Emmerie-Engel procedure has been developed for the estimation of tocopherols in blood plasma (297) and in milk (294). In this procedure mild hydrogenation is employed to remove interference due to vitamin A, carotene, and other unsaturated substances which react with the Emmerie-Engel reagent. A molecular distillation procedure (296) is applicable to the analysis of food fats.

Upon treatment with nitrous acid, β-, γ-, and δ-tocopherol (but not α-tocopherol) form yellow nitrosotocopherols which are soluble in petroleum ether and can be separated chromatographically, thus forming a basis for their differential analysis (295). In mixtures with α-tocopherol, the latter is estimated by difference from the total tocopherols, determined by a modification of the Emmerie-Engel procedure.

Applications of the thiochrome reaction to the estimation of thiamine in beef (166) and cereal products (137, 169) emphasize the need for the zeolite adsorption step in the purification of the thiamine extracts. However, special adaptations of this reaction for the determination of thiamine in milk (171) and cereal products (327) dispense with this step. In the case of milk, free thiamine is liberated by takadiastase digestion and determined in the filtrate after precipitation with 2% trichloroacetic acid. In the analysis of flours, extraction with hot 2% acetic acid is claimed to be an improvement over acid potassium chloride extraction, which makes possible the elimination of zeolite adsorption (327). Preliminary digestion with takadiastase is recommended for baked products analyzed by this simplified procedure. The so-called red-dye method has been adapted to the rapid determination of thiamine in cereal products (169), but this procedure is not recommended for beef, eggs, or other high protein–low thiamine foods.

The use of fluorometry in various vitamin assays has recently been reviewed (212). Investigations designed to improve the extraction and reduce the effect of interfering pigments in the fluorometric estimation of riboflavin have extended the usefulness of this procedure. Adaptations have been described for meat (230, 264), feed materials (91, 313), and eggs (288). Improvement in the fluorometric methods of Najjar (338) and Hodson and Norris (333) have been reported. Both methods use an internal standard and employ potassium permanganate in the oxidation of interfering substances. Furthermore, by the use of hydrochloric acid–acetone as the extracting agent and clarification of the extract with Celite filter aid (333) the applicability of the fluorometric method has been extended to include a variety of highly pigmented materials. Good agreement is reported with microbiological determinations.

The specificity of the dichloroquinonedichloroimide reagent for pyridoxine in biological and pharmaceutical materials has been improved by the introduction of borate into the reaction system. This renders the pyridoxine nonreactive, and thus provides a correction for interfering substances (170). The specificity of this reaction for pyridoxine limits its value in the estimation of the vitamin B₆ content of natural materials, which also contain the other forms of the vitamin, pyridoxamine, and

pyridoxal. Thus a microbiological procedure is preferred for the estimation of total vitamin B₆ activity.

The determination of nicotinic acid in cereals and other food by the cyanogen bromide–p-aminoacetophenone method has recently been reviewed (192). A modification of the colorimetric method for nicotinic acid (37) is described in which hydrochloric acid is added to the sample before addition of the reagent; under these conditions, it is said to be possible to avoid two blanks, one for the reagent and one for the sample. It has been pointed out (263) that in the presence of ammoniacal buffer the cyanogen bromide reaction takes place without the addition of an organic amine. Greater sensitivity and precision as well as a saving of time are claimed for this modification of the color reaction.

The ultraviolet absorption maximum (325 mµ) for choline reineckate in acetone solution is suggested as the basis for estimation of choline (384). An improvement in the specificity of reineckate methods has been described (350) in which the derivative is treated with dilute alkaline permanganate and converted to trimethylamine. A high degree of specificity is claimed for this procedure. A chemical method for pteroylglutamic acid has been reported (188) which is not sufficiently sensitive for this vitamin in natural materials but is applicable to certain pharmaceutical preparations. It is based on reduction with zinc dust to an aromatic amine which is estimated by a diazotization and coupling reaction.

Various recommendations have been proposed to avoid nonspecific reduction in the chemical estimation of ascorbic acid. The advantages and limitations of oxalic acid as an extractant for ascorbic acid have been discussed (386). The slurry prepared from 1 part of vegetable and 4 parts of 0.5% oxalic acid is said to be stable for a period up to 2 weeks (140). The indophenol-xylene extraction procedure has been applied to the determination of ascorbic acid in fresh and prepared fruits and vegetables (250, 268, 314). Miller (250) points out that nonspecific reducing substances develop more rapidly on storage in foods of low ascorbic acid content than in those of high content. Improved specificity in the indophenol-xylene extraction method is obtained by application of the formaldehyde condensation reaction which, by preventing the reducing action of ascorbic acid, provides a basis for correcting for the action of reductones (311). In the analysis of fruit products the addition of 3% hydrogen peroxide is used to overcome the interference due to sulfite, iron, and tin (314). A method has been described (347) wherein ascorbic acid and interfering substances are enzymatically oxidized by a cucumber juice extract and the dehydroascorbic acid is specifically reduced to ascorbic acid by a suspension of Escherichia coli or Staphylococcus albus, following which the indophenol titration is employed. Advances have been reported in the application of the 2,4-dinitrophenylhydrazine method for ascorbic acid (251). The use of a 540 mµ filter is advised in the analysis of plant and animal tissues, and the necessity for the inclusion of thiourea in the reaction is emphasized.

A polarographic method has been described for the estimation of vitamin C in a variety of fruits and vegetables (136). Under some conditions, such as when the limiting current is not well defined, corrections are necessary to determine the true diffusing current. It is claimed for the polarographic method that after the initial calibration no standardization of solutions is required and the method can be applied in colored solutions containing suspended matter. Because ascorbic acid determinations are often used as a means of determining losses in processing or cooking of vegetables, it is pertinent to cite several papers (221, 262) that recommend the use of alcohol-insoluble solids as a reference base. Computations based on total solids are erroneous in view of their altered composition after cooking.

A colorimetric method is described for the determination of flavanones in grapefruit and other citrus fruit (93). Some question may be raised as to the specificity of this reaction, which

is based on the addition of strong sodium hydroxide to the diethylene glycol solution of "crude flavonones."

Microbiological Assays for the Vitamins. As in the case of the amino acids, a considerable number of papers have appeared during the past five years directed toward improving the specificity and range of applicability of microbiological assays for the vitamins. Some are based on changes in the technical details of earlier methods, in the preliminary hydrolytic procedures, in the composition of the media, or in conditions of incubation. Others involve the use of microorganisms hitherto not used for the specific vitamin in question. A recently published symposium contains chapters by specialists reviewing the microbiological (as well as other) methods for the various vitamins (*92*).

Although most workers prefer the thiochrome or red-dye methods for the estimation of thiamine, improvements in microbiological methods have been described based upon macrofermentation with yeast (*334*), on the growth of *Lactobacillus fermenti* 36 (*67*) and of the fungus *Phycomyces blakesleeanus* (*87*). In the case of riboflavin most food analysts seem to prefer modifications of the fluorometric method, although the official microbiological procedure has many adherents because of its unquestionably greater specificity. A recent microbiological assay for riboflavin employs *Leuconostoc mesenteroides* 10,100 which is claimed to be 50 times as sensitive as *L. casei*, the organism used in the U. S. Pharmacopoeial assay (*213*). Improvements in the media for the *Lactobacillus arabinosus* 17-5 assay for nicotinic acid have been reported (*22, 320*); the latter involves the use of Lloyd's reagent-treated peptone, liver, and yeast mixture for the removal of traces of nicotinic acid. *Acetobacter suboxydans* (*206*) and *Proteus HX* 19 (*148*) have also been used in the microbiological estimation of nicotinic acid. A yeast (*Torula cremoris* 2512) assay for nicotinic acid has been adapted to the differential assay for nicotinic acid (or its amide), trigonelline, and N'-methylnicotinamide by varying the conditions of hydrolysis (*379*).

Of critical importance in the estimation of vitamin B_6 in natural materials is the hydrolytic procedure employed as well as the choice of test organisms. Following the observation (*242*) that 2 N sulfuric acid extracts only part of the total vitamin B_6 activity of yeast (according to the *Saccharomyces carlsbergensis* assay), it was shown (*315*) that 0.055 N sulfuric acid was a more efficient extractant. This has been confirmed by subsequent work (*299*) in which autoclaving at 20 pounds pressure for 5 hours in 0.055 N sulfuric acid is recommended as a general extraction procedure. In addition to *Saccharomyces carlsbergensis* (*174*), *Streptococcus faecalis* has been proposed as a test organism for pyridoxal and pyridoxamine (*300*). In this method the medium has been improved by the substitution of sodium citrate for sodium acetate and the addition of sterile cystine. The same investigators also propose an improved *Lactobacillus casei* assay for the estimation of pyridoxal (*298*).

Because of the question surrounding the completeness of extraction of natural materials for microbiological or chemical assay, the animal assay for vitamin B_6 continues to play an important role. An improved rat assay has been described (*321*) in which a striking difference in response is obtained depending on whether the vitamin derivative is fed in the diet or administered by dropper or injection. In the latter case, pyridoxine, pyridoxal, and pyridoxamine all have approximately the same potency; but when included in the diet, pyridoxine is more active than the related compounds. For the release of bound pantothenic acid in natural materials, a short incubation with Mylase P is adequate provided that a sufficient quantity of the enzyme is used (*52, 190*). *Lactobacillus arabinosus* 17-5 is claimed to be a better microorganism for pantothenic acid assays (*167*) than *Lactobacillus casei* because the latter is more sensitive to the interfering effects of fat, starches, etc. A yeast assay has also been adapted for this vitamin (*17*). The interfering effects of lipoidal growth stimulants in the *Lactobacillus casei* assay for biotin has been

investigated in particular relation to the assay of rice-polish extract (*356, 378*). The cholineless mutant of *Neurospora crassa* has been employed in the estimation of biotin as well as of choline in milk products (*172*).

Because biotin is the first vitamin for which such a method has been described, it is of interest to refer here to the agar plate method recently proposed by several groups of workers in this country and in England. In its application to biotin assay (*134*) filter-paper disks are inoculated with doses of the standard and the unknown and are placed on agar plates seeded with the test microorganism, *Lactobacillus arabinosus* 17-5 or *Saccharomyces cerevisiae*. The diameter of the observed zone of growth is a linear function of the logarithm of the dose over a wide range— 1 to 1000 micrograms per ml. This procedure is claimed to be as sensitive as those using liquid media and would seem to have as wide application in other assays for growth stimulants as it has had in the evaluation of antibiotics where it is applied as a "zone of inhibition" procedure.

The microbiological estimation of folic acid has been the subject of recent collaborative studies (*123, 124*). Satisfactory results have been reported using either *Streptococcus faecalis* or *Lactobacillus casei* as the test organism. A modified medium is recommended which is applicable to either organism. Dehydrated bacteriological media are available commercially for the assay of various vitamins, and recently such a medium has been described for the folic acid assay (*59*). For the liberation of bound folic acid (vitamin B_c conjugate) prior to microbiological assay, enzymatic digestion with extracts of hog kidney or chicken pancreas is employed (*33, 51, 277*). This procedure is not applicable to plant extracts.

At the present writing great interest attaches to the development of a microbiological assay for the so-called animal protein factor (now believed to be identical with vitamin B_{12}). Indications are that a strain of *Lactobacillus leichmannii* will be found to serve as suitable test organisms for this factor (*205, 341, 390*).

Biological Assays for the Vitamins. The only major innovation in the biological assay for vitamin A during the past five years has been the introduction of a liver-storage test (*149*) based on the colorimetric estimation of the vitamin A deposited in the liver of previously depleted rats following the administration of test and standard doses. The quantitative aspects of this assay have recently been improved (*128*) in part through a simplified variation of the antimony trichloride method adapted to 1-gram samples of liver tissue (*131*). The principal advantages of the liver-storage method are the short depletion period (which avoids gross pathological changes in the animal) and the short test period. The fact that the size of the dosage levels limits the method to test materials containing at least 3000 units per gram restricts the usefulness of this otherwise promising method.

Little has been done to improve the official U.S.P. bioassay for vitamin D. It has been proposed (*129*) that the recognized deficiency of protein in the basal ration be corrected by supplementation of the diet with lysine. By this means better growth has been achieved in some laboratories (including the author's) but not in others. Currently, revision of the U. S. Pharmacopoeial bioassays for both vitamins A and D is under consideration. Various proposals have been studied for the improvement of the A.O.A.C. chick assay for vitamin D_3 (*118, 202*). As a result of an extensive collaborative study of several improved rations for the chick assay of vitamin D (*34*), no recommendations could be reached for a dietary change which would result in improved precision of the method. The shorter and less laborious toe-ash method has found favor at the hands of recent investigators (*57, 245*) and is supported by comparative studies of it, the bone-ash method, and the roentgenographic method based on measurements of the tarsal-metatarsal distance. An assay based on the use of turkeys as test animals has been reported (*375*).

In view of the multiform nature of various vitamins as they occur in animal and plant sources, it is highly pertinent to inquire

whether extraction methods and chemical reactions, however specific they may be, can be relied upon to measure the physiologically available vitamin content of such materials. Hence, methods for biological assay continue to serve a very important function. Because species differences are known to exist in the response to various forms of a given vitamin, considerable interest attaches to the use of man himself as a test animal in gaging the physiological availability of vitamins in foods and pharmaceutical products (243, 279).

INORGANIC ELEMENTS

For the spectrographic determination of metallic elements in foods, a buffer solution has been developed which eliminates the effect of variable amounts of the alkali and alkaline-earth elements (43). By this means manganese, iron, aluminum, copper, tin, and lead have been estimated in a single sample with a precision of ±10%. The preferred colorimetric reagent for the estimation of iron in foods appears to be α,α'-dipyridine (186, 316, 385), although potassium thiocyanate and 1,10-phenanthroline continue to have their adherents (289, 353). Dry ashing is generally preferred; however, a simplified adaptation for the determination of iron in milk is described (316) in which ashing is avoided entirely, and the determination is conducted directly on the filtrate after precipitation with a hydrochloric acid–trichloroacetic acid solution containing thioglycollic acid. Despite the high values for the iron content of milk which continue to appear in food tables, surveys of raw milk on the American market in recent years reveal an average iron content of 0.32 mg. per kg., the values ranging from 0.114 to 0.650 (198, 199). This discrepancy reflects in an interesting way the improved precision of modern colorimetric methods for trace elements as well as the effort to avoid metallic contamination in the modern handling of milk.

Recent modifications of the dithizone method for the determination of copper in foods are based upon the extraction of the dithizonate complex from aqueous solution at pH 2.3 and destruction of the reaction products of remaining interfering metals by shaking with acid potassium iodide solution (26, 258). Certain objections to this method have been overcome without sacrificing sensitivity by measuring the optical density at two wave lengths, 520 and 625 mμ, instead of the former alone (146). However, this is achieved at the loss of some of the simplicity of the earlier procedure (25). In connection with the colorimetric or polarographic methods for estimating copper in milk fat, an improved technique has been described for charring large samples of fat prior to ashing (78).

A microcolorimetric method for manganese, sensitive to 0.02 to 0.5 microgram per ml. of solution, is based upon periodate oxidation to permanganate and subsequent development of a yellow color by reacting with 4,4-tetramethyldiaminotriphenylmethane (132). An even more sensitive method is based on the fact that the rate of oxidation of diethylanaline to a yellow dye by potassium periodate is a function of the Mn^{++} concentration (217). Mention may again be made of the microbiological method for manganese based on the requirement of *Lactobacillus casei* for this element (29).

A modification has been described (125) of an earlier method (362) for the estimation of potassium in foods and other biological materials based on its precipitation as potassium phosphotungstate. The flame photometer is coming into use for the estimation of the alkali metals, and papers have described its application to food analysis (153, 357). A colorimetric method for trace amounts of magnesium is based on the reaction with thiazole yellow (98). An improved dithizone procedure for zinc in foods has been reported (5, 14). Volatile sulfur, as estimated photometrically, is said to be correlated with the pungency of onions (90).

Numerous papers have appeared on the determination of

metallic elements *present as* normal constituents or contaminants in foods. During the past five years papers have been reported on arsenic (235), antimony (229), bismuth (187), boron (18, 130, 339), cadmium (70), cobalt (16), lead (72, 200), mercury (71), selenium (218), tin (139), and uranium (270). Recent papers have described the determination of trace quantities of fluorides (210, 376) and iodine (344) in foods. The method for fluoride is based on distillation over sulfuric acid followed by evaporation of the distillate in an alkaline fixative and subsequent ashing. The ash is redistilled with perchloric acid and silver sulfate and the distilled fluoride ion is back-titrated in the presence of alizarin red and thorium nitrate solution.

DECOMPOSITION AND CONTAMINATION

Among the methods recently proposed for the detection of spoilage in sea foods are the simple determination of the pH of muscle tissue (111), the estimation of volatile reducing substances by aeration through alkaline potassium permanganate (220), the determination of histamine content by a pharmacological procedure based on contraction of the guinea pig intestine (133), and the colorimetric determination of the indole content of the tissue by means of the p-dimethylaminobenzaldehyde reaction applied to the steam distillate (24, 101, 209). In a comparative study of chemical methods for evaluating the quality of fish (335) it has been shown that determination of the total volatile acids or of trimethylamine furnishes an indication for fish stored above 0° C., but below that temperature the products of protein degradation or of oxidation of the fat furnish more reliable information (335). The freshness of canned herring has been estimated from the acid value of its oil content (66) and more recently, as in the case of canned salmon (64), from the carbon dioxide—i.e., volatile acid—content of the drained muscle tissue (65). The volatile acidity is measured by means of a microdiffusion procedure (83). Details are given of a shear-testing device for measuring the changes in the texture of dehydrated fish on storage (69). On the reasonable supposition that the indole resulting from protein decomposition is derived from tryptophan, an analytical method has been developed for the free amino acid in milk, cream, and butter as an index of early putrefaction (100).

Several papers have described methods for the detection of excretory contamination in foods. The presence of uric acid in eggs is regarded as an indication of contamination with chicken manure. A method for its determination is based upon selective extraction of the uric acid by quinoline (99). In the place of the fluorescence test for rodent urine on bagged commodities, a simple spot test for urea has been suggested (49). This is performed by brushing an alcoholic solution of p-dimethylamino-benzaldehyde and oxalic acid over the suspected area. It has also been proposed that fecal contamination in foods be detected through the presence of the fecal enzymes trypsin and alkaline phosphatase (85). As evidence of fecal pollution, foods and water have been analyzed for hydrogen sulfide by distillation in an inert atmosphere and titration with ammoniacal silver nitrate using p-dimethylaminobenzalrhodanine as an external indicator (96). Confirmation of the specificity claimed for this novel approach would seemed to be desired.

Following the publication of the manual of the U. S. Food and Drug Administration on the identification of filth (rodent hair or excreta, insect fragments and excreta, etc.) (361), much of it was incorporated in the book of methods of the Association of Official Agricultural Chemists (12). Among papers describing flotation or separation procedures adapted to specific foods are those on alimentary pastes (157), flour (366), and ground spices and chocolate products (367). It has been suggested that microscopic examination of the isolated foreign matter can be facilitated by throwing the image on a screen (208).

As a means of determining the adequacy of heat treatment of

foods, methods for the determination of residual enzymatic activity have been employed. For example, the estimation of the peroxidase activity is used to determine the efficiency of blanching in frozen vegetables (15, 240); the phosphatase test is applied in milk cheese, and other dairy products (183, 214, 317–319) to control pasteurization; and the detection of urease activity of soybean meal provides an index of the adequacy of heat-processing (32).

The deterioration of certain foods in storage is associated with an increase in the fluorescence of extracts prepared therefrom. This appears to be due in part to sugar–amino acid reaction products as evidenced by the fluorescence of saline extracts, and in part to the product of the reaction of lipide amines with aldehyde, so-called lipide fluorescence as observed in ether or acetone extracts (36). Similar observations have been reported for milk products in which the major source of fluorescence—viz., that due to riboflavin—is differentiated from that due to sugar–amino acid reactions and to the lipide amine–aldehyde reaction (194). Fluorescence studies have been reported on milk (285), egg powder (286), and various other foods (284). That such fluorescence may be of complex origin is indicated by later observations—for example, the fluorescence of saline extracts of dehydrated egg powder is correlated closely with the loss in palatability of high (4 to 5%) moisture products but poorly when the moisture content is below 2%. However, correlation of lipide fluorescence with loss of palatability is good regardless of moisture content (36).

DISINFECTANTS, PRESERVATIVES, INSECTICIDES

The generally accepted method for the determination of quaternary ammonium compounds in foods is based on their reaction with ferricyanide (158, 381, 382). The quaternary base is precipitated as the salt of ferricyanic acid and the excess uncombined ferricyanide is measured iodometrically in acid solution. Methods for the estimation of this preservative in table sirups, bottled fruit-juice beverages, beer, etc., have been reported, and their applications to salad dressings, relishes, etc., are being studied.

A rapid, direct titration method for sulfur dioxide in dehydrated foods is said to give good agreement with distillation and polarographic procedures (292). Its application to frozen fruits involves extraction in buffered sodium chloride solution to stabilize the sulfur dioxide against enzymic oxidation, alkalinization of the filtrate to liberate combined sulfur dioxide acidification, and titration with iodine with and without added formaldehyde. A high degree of reproducibility is claimed for this procedure (290).

The use of DDT, hexachlorocyclohexane (benzene hexachloride), and similar compounds as sprays on fruit, in barns, etc., has made it imperative that methods be developed for their determination in canned fruits and vegetables, dairy products, etc. Of the various methods studied in this connection (372), colorimetric analysis involving intensive nitration and the development of colored nitration products by reaction with methanolic sodium methylate in benzene (325, 326) appear to be most favored. Modifications of this procedure have been described for the determination of DDT (or its residue) in canned foods (359) and in milk and butterfat (77). A method has also been described for the determination of DDT in the presence of DDD based on the specific reaction of xanthydrol-pyridine–potassium hydroxide reagent with DDT (73, 348). In the absence of DDT, as indicated by the latter reaction, hexachlorocyclohexane has been determined by extraction with ether, dehydrochlorination with monoethanolamine, and determination of the separated chloride (185). Partition chromatography has been applied to the separation of the hexachlorocyclohexane isomers (304). Diphenyl and o-phenylphenol have been determined in oranges wrapped in paper treated with these fungicidal agents (355).

MISCELLANEOUS

The evaluation of color by visual inspection or by comparison with standard glasses or inorganic solutions is being replaced by the newer photometric and spectrophotometric procedures. This is illustrated in papers on the estimation of the color of fish liver or vegetable oils (1, 48, 371) and corn sirup (323). A series of reports giving spectrophotometric data on the certified food colors provides valuable aid in their identification and estimation (75, 271–273).

There is a growing tendency to introduce greater objectivity into the measurement of the color of canned foods. The color of tomatoes, beans, beets, and carrots has been standardized by comparison with colored disks in a Keuffel and Esser disk colorimeter or by means of spectrophotometric absorption measurements of extracts prepared with appropriate solvents (215). Similarly spectrophotometric and fluorometric measurements have been applied to the evaluation of the pigments of peaches and apricots as an index of their degree of ripeness (216). By means of a reflecting attachment to the Beckman spectrophotometer, the color of opaque materials such as evaporated milk has been measured for standardization and control purposes (267).

Methods for the estimation of fat (crude lipide) have been adapted to such foods as cream and ice cream (211), vegetable matter (274), meat (115), and citrus juices (50, 352). The development of off flavor in processed orange juice is attributed not so much to the peel oil in the juice as to the suspended matter which contains the lipide fraction (89). Micromethods for the estimation of fatty acids (322), for the determination of the saponification number of fats and oils (239), and for the partition of phospholipide mixtures (328) have recently been described. Physical and chemical methods are proposed for the characterization and evaluation of peanut butter (363). An antimony trichloride procedure is described for the detection of tung oil as an adulterant in higher-priced, edible oils, and a gravimetric, nitric acid oxidation is used for its estimation (351). It has been claimed that the constants for pure olive oil can be used as the basis for detection of adulteration in oil-packed sardines (365). A method has been described for the estimation of the free fatty acids which develop in dried egg powders on storage (196). Cholesterol determination is used for estimating the degree of contamination of egg white with egg yolk (84). It is sometimes necessary to differentiate between egg and soybean lecithin in alimentary pastes. A proposed method for accomplishing this objective is based on the strong fluorescence of soy lecithin in ultraviolet radiation (383).

Among the recent methods proposed for the determinations of soybean flour in meat products is a highly specific serological procedure using the serum of sensitized rabbits (154). Of the chemical methods, that based on the estimation of glycinin, the characteristic globulin of soybean (19), and those based on the determination of the hemicellulose content (28) appear to be the most promising.

Data have been reported on the estimation of tomato solids in ketchup on the basis of the acidity and lead numbers (aqueous and acetone) of tomato purée (257).

Several new analytical methods are of special interest to cereal and feed chemists. A spectrophotometric method for the estimation of extractable gossypol in cottonseed meal is based upon the characteristic red color (absorption maximum 510 to 520 mμ) of the reaction product with antimony trichloride (35). An improved method for the rapid estimation of bromates in bromated flour is based upon spectrophotometric measurement of the starch-iodine color developed in an extract containing the bromate (197). A method for the determination of the proteolytic activity of flour and related products employs hemoglobin as the substrate; estimation is made of the nonprotein nitrogen in the filtrate after digestion under controlled conditions (248). The detection of milk powder in flour has been effected by lactose determination (94).

In the analysis of vanilla extract and imitations thereof, advantage is taken of the ultraviolet absorption maxima for vanillin and coumarin (114). The readings are made on the ether extract of the filtrate after precipitation with lead acetate. A later spectrophotometric procedure for vanillin is based on absorption in the range 328 to 370 mμ before and after treatment with alkali (222). A color test has been proposed for foreign resins (such as those of wild cherry bark and St. John's wort) in vanilla extract (112).

A recent method has been proposed for the determination of chlorogenic acid content of coffee (256) in which use is made of the ultraviolet absorption maximum (325 mμ) of this compound. It gives values slightly higher than the iodometric method for green coffee and about 17% lower for roasted coffee: however, it is claimed to be more specific than the iodometric method.

Silicotungstic acid is claimed to be superior to other protein precipitants for the determination of gelatin in ice cream (252). Apparatus for the collection and analysis of gases in vacuum-packed food containers has recently been described and is claimed to permit the determination of the composition of as little as 1 cc. of gas (61).

CONCLUSION

An appropriate note on which to end this review would appear to be a word of tribute to the many chemists who give so unstintingly of their time in collaborative studies of new analytical methods. It is they who are ultimately responsible for the useful manuals published by such groups as the Association of Official Agricultural Chemists (12), the Association of American Feed Control Officials (11), the American Dairy Science Association (10), the American Association of Cereal Chemists (8), the American Oil Chemists' Society (9), and the Association of Vitamin Chemists (13). These handbooks are indispensable armamentaria of analytical chemists in their respective, special fields.

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SOLID AND GASEOUS FUELS

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IN only a few cases do single publications on fuel analysis indicate the state of the art as of our base line, which is taken as January 1, 1943. Thus, in the sampling and analysis of coal and coke the reader may refer to A.S.T.M. Standards (8) for the methods generally accepted in 1942. No similar standards are available for the analysis of gaseous fuels, but Altieri (3) in 1945 discussed gas analysis and testing of gaseous materials. The present review includes a bibliography of all references the authors

have been able to find, but discusses in the text only the more important developments during the past five years. The subject naturally breaks down into three sections: solid fuels, gaseous fuels, and liquid products derived therefrom.

SOLID FUELS

This section discusses the sampling and analysis of coal, coke. wood, charcoal, and briquets.

SAMPLING

A chemical analysis is generally made on a small amount of material; the results are expected to represent precisely the composition of a large quantity of the same material. Obviously, then, the sampling procedure must be of such a nature that the final small laboratory sample will be of the same composition as the large mass sampled. For many years, in order to accomplish this result in the case of coal, very large samples (1000 pounds or more) were taken. During the past 15 years many studies, made in this country and in England on the theory of sampling and the factors involved in proper sampling of coal, indicated that the accuracy of sampling was influenced by the size consist of the coal and the amount of mineral matter present. In consequence of these studies the American Society for Testing Materials provided an alternate method of sampling which varied the minimum weight and number of increments to be taken with the size groups and ash content. This greatly reduced the sampling labor, for in the case of size group, $5/8$ inch and under coal with less than 8% ash, only 15 increments of 2 pounds each need be taken.

Landry (115) in a comprehensive mathematical study discusses the following factors pertaining to coal sampling: variability of ash content of coal, theory of random sampling, sampling characteristics of a multiple size coal, theory of orderly sampling, and coal sampling specifications.

In a further study (114) he concludes that the data needed to supply information for coal sampling are size consist, variability of the ash of pieces by float and sink methods and by direct analysis, variability of the ash of increments, and collection and analysis of gross samples of specified number of increments of constant weight. Examples are given of a log-log representation of data that can be used to determine the number and weight of increments of various sizes of coal of different ash content that can be used in the collection of gross samples. From these studies one may conclude that the present A.S.T.M. procedure errs on the side of conservatism. However, many more sampling studies will be necessary before further simplification of sampling procedure will be justified.

Visman (207) gives a formula for the number and weight of increments required for a given accuracy, using sampling constants based upon the amount and nature of ash and method of reduction, and Budryk (35) suggests that the factors concerned show a wide variation in different coal-producing countries.

Fitton and Rogers (75) performed experiments to determine the magnitude of errors involved in sampling pulverized coal in (a) a bin and feeder, and (b) a unit pulverizing system. In (a) sampling presents little difficulty, for any method in which the fuel is sampled by increments gives a representative sample; but in (b) appreciable errors attributable to unsuitable sampling tubes may arise. Theoretically, the stream lines should not be disturbed by sampling; nevertheless, for fine coals, the errors with a straight tube were smaller than might have been expected. There was a greater variation in the error of concentration than in the error of fineness. Errors due to sampling at wrong velocity are particularly great with coarser fuels, and in general it is better to sample at too high a velocity than at too low.

Cooper et al. (47) studied the loss of moisture in crushing tipple samples and showed that the type of coal and total moisture content influence the rate of loss. The average loss was 0.15%.

Shchlukin (177) in preparing coke samples for analysis first splits the sample into classes according to size, after which each class is weighed and the percentage of each in the mixture is calculated. Increments are then taken from each class in proportion to its amount in the total.

The contamination of samples by grinding equipment was studied in the case of phosphorus by Jones (107). Little pickup was shown by use of mills, bucking boards, and iron pounders on iron plates or concrete on reduction to −14 British standard sieve. Fine grinding to −72 B.S. sieve showed a pickup of 0.0044% phosphorus in chrome-iron and iron equipment. Fine pulverization is best accomplished by stamping in a manganese steel mortar.

In the matter of equipment Powell (147) describes a laboratory sampler in which a thin stream of crushed coal or coke runs from a hopper into twelve triangular radially arranged receivers mounted on a table turning at 60 r.p.m. If the bulk sample takes 5 minutes to run from the hopper, the sample in each receiver is made up of 300 increments selected automatically.

Mott and Spooner (133) describe methods of drying and grinding coal for preparation of −72 B.S. sieve samples.

A sample of 14 pounds of −0.5-inch wet or dry coal is ground to −0.25- to −0.125-inch with a Carr crusher and reduced to 2 pounds by riffling. If the coal appears wet, surface water is then flashed off at the rate of 1% per minute at 200° C. with coal layers of 0.7 gram per sq.cm. A Christie and Morris mill is used for the final reduction. The total time of preparation from a 66-pound gross sample is estimated at 16 minutes. The Carr crusher is described in detail.

PROXIMATE ANALYSIS

Brown and Bean (33) review the entire field of proximate coal analysis. The determination of moisture, ash, volatile matter, and coking properties is considered and the prediction of industrial performance from a proximate analysis is discussed.

Belcher and Spooner (18) describe apparatus and technique for the microanalysis of solid fuels. The only common determination made on solid fuels for which a micromethod is not available is that of the calorific value, which is being investigated by the authors.

Moisture. The problem of speeding up the determination of moisture in coal continues to attract attention. Liplavk (120) employs a high-frequency current to heat 5-gram samples of coal suspended on a torsion balance to temperature not exceeding 120° to 130° C. The accuracy of the determination is claimed to equal that of the xylene distillation method and the time of a determination not to exceed 8 minutes. Simon (186), using an apparatus similar to the A.S.T.M. apparatus for determining moisture in oils, performs a xylene distillation determination in 0.75 hour. Winkler (209) claims the Brabender apparatus can yield satisfactory results if proper precautions are taken.

There has been much interest in the question of the condition of water in coal. Schmidt and Seymour (163) determine the "surface moisture" of coal by treating the sample with ethyl or isopropyl alcohol, filtering, and determining the water in the alcohol by the change in specific gravity. Dunningham (58) determines the "inherent moisture" (defined as the maximum moisture which the coal will hold at 100% humidity and atmospheric pressure) by a new procedure.

Commercial coal samples are crushed and graded to required sizes. Each size is separately floated at 1.35 specific gravity in carbon tetrachloride–benzene mixture and the floated samples are air-dried until free from odor. Approximately 150 grams of graded coal and 30 ml. of water are rotated occasionally in a stoppered bottle to wet the coal thoroughly. After 48 hours the coal is drained on a 20-mesh gauze and transferred to a bottle lined with filter paper. This treatment is repeated in bottles with fresh filter paper, four times with 0.25- to 0.125-inch coal and five times with 0.125- to $1/16$-inch coal. Moisture is then determined on the samples at 105° C. and the two sets of data are averaged. The earlier method was to equilibrate the sample by exposing it to solutions with a vapor pressure equivalent to just under 100% relative humidity (Stansfield).

Dulhunty (57) claims determination of the maximum inherent moisture in coal by a controlled evaporation of the adherent moisture in a saturated atmosphere at constant temperature in air.

Volatile Matter. Zhukovskaya and Shenberg (210) determined the yields of volatile constituents from all kinds of Donetz coals by the use of a platinum crucible over a Bartel burner and compared results with those obtained with a porcelain crucible in a

crucible or muffle furnace. Results obtained by the two methods were in good agreement.

Newworth and Kirner (136) report a micromethod for the determination of volatile matter in coal. The sample is carbonized in dry oxygen-free nitrogen in a platinum boat placed in a quartz combustion tube.

Spooner (190), extending previous work (191) to coals containing more than 10% oxygen and showing presence of durain or fusain, revised the oxygen factor in the modified Dulong formula (132). The best expression for volatile matter for the whole range of coals from peat to anthracite is $V = 12.6H + 120 - 41.8$ when H is greater than 4.2%. Presence of durain or fusain caused large negative deviations between calculated and experimental results. Special formulas are given for less than 4.2% H for volatile matter, gaseous, and liquid hydrocarbons.

Selvig (172) analyzed statistically results of duplicate determinations of volatile matter of 100 samples of each of anthracite low-temperature coke, and subbituminous coal. Bureau of Mines procedure for determination of volatile matter gave results meeting A.S.T.M. permissible differences 95% of the time for anthracite and subbituminous coal. The permissible difference for low-temperature coke is too stringent. The following permissible differences between duplicate determinations of volatile matter are recommended: anthracite 0.3%, low-temperature coke 0.5%, and subbituminous coal 0.7%. A change to a 10-ml. platinum crucible with capsule-type cover and an electrically heated vertical-tube furnace is recommended.

Ockelford (137) designed a furnace to meet the British standard specifications for determination of coal volatile matter—i.e., 925° C. working temperature, a zone of constant temperature, and a given rate of temperature recovery after the insertion of the silica crucible containing the sample.

The standard method in Belgium for determination of volatile matter in coal is the double crucible method (161). The following factors were investigated: nature and dimensions of the crucibles, method of heating, time and temperature of heating, atmosphere, mesh size, and weight of sample used. The results indicate the necessity of maintaining fixed working conditions in the method for the determination of volatile matter in coal.

Suvorovskaya (197) claims that porcelain crucibles and an electric furnace can be substituted for the conventional platinum crucibles over a gas burner in the determination of volatile combustible matter in fuels.

Reynolds and Holmes (151) describe the apparatus and procedures used in the coal carbonization laboratory of the U. S. Bureau of Mines.

Ash. Kistyan (111) determined the ash content by passing oxygen through an electric furnace heated to 1000° C. countercurrent to boats carrying the coal, thereby shortening the time of combustion to 10 to 20 minutes. Edwards and Pearce (60) claim that as much as 60% of the potassium and sodium is lost by the usual open ignition as compared with ignition in a bomb.

ASH SOFTENING TEMPERATURE

The U. S. Bureau of Mines (205) conducted a cooperative investigation of the effect of furnace type and atmosphere on the fusibility of coal ash. Sixteen laboratories using standard methods and four types of gas furnaces burning natural and manufactured gas and two types of electric furnaces with different methods of maintaining a reducing atmosphere tested fusibility of coal ash. The Barrett furnace for both natural and manufactured gases gave lower results than the Denver fireclay of Melter's No. 3 furnaces. The differences were within the tolerance allowed between different laboratories. At lower temperatures manufactured gas gave lower results than natural gas and higher results at higher temperatures. The Baker electric furnace, with its constant composition of atmosphere, gave lower results than gas furnaces using natural gas. The differences among the several types of furnaces and atmospheres are believed to be due to the differences of the oxidizing and reducing conditions surrounding the cones.

Endell et al. (62) used an electron microscope for which an arrangement was developed for electrically heating the substance to be examined. The calibration is given by the melting point of definite substances and the respective heating current. Ashes of lignites and coals were examined at a magnification of 2500 as to their melting behavior at high temperatures from beginning of sintering to complete flowing at 1600° C.

Hohlfeld (103) gives a review of ash softening curves and describes their peculiarities in relation to ash composition.

Rousseau and Delorme (156), by curves of deformation of fuel ash as a function of temperature, show that, on heating progressively, fuel ashes exhibit four distinct zones: an expansion zone, rarely extending beyond 1000° C. and offering no special feature; a fritting zone corresponding to a progressive darkening in color and a considerable reduction in volume, the texture increasing in compactness and coherence with increase of temperature; a reaction zone in which acid and basic constituents react with one another to form a blackish glass, the zone being the seat of a marked exothermic phenomenon and its range in temperature varying with different ashes and possibly as great as 130° C.; and a zone of flow where the viscosity gradually decreases in the same manner as ceramic products that are heated progressively. Micrographic examinations showed that in the fritting zone there are local fusions of disseminated compounds which agglomerate the solid constituents; these fusions increase in number with rise of temperature. Adhesion tests revealed the temperature at which the constituents possess sufficient agglutinating power to become welded into a solid block. In all cases the initial temperature of definite adhesion practically coincides with the beginning of the expansion anomaly on the curves—i.e., the beginning of the reaction zone—which is therefore the temperature at which clinkering begins to form.

Zinzen (212) from his investigation on fusion behavior of fuel ashes concludes that their principal softening point is not the decisive factor in the sintering process, as the latter is influenced by other processes which take place below the fusion temperature, especially the formation of sulfides by reduction.

CALORIFIC VALUE

The only completely satisfactory method for the determination of the heating value of a coal or coke consists of burning the sample in a calorimetric bomb. As this method is time-consuming and requires close attention to detail, empirical formulas have been developed to calculate the calorific value from the proximate or ultimate analysis of the fuel. All these methods are subject to more or less error when applied to all ranks of coals. Although a number of contributions have been made during the past 5 years, none contributes any new concept to the solution of this problem.

ULTIMATE ANALYSIS

Carbon and Hydrogen. The standard procedure for determination of carbon and hydrogen involves combustion in oxygen followed by absorption of the carbon dioxide and water formed. In order to shorten the time and decrease the size of sample necessary some work has been reported on micro- and semimicromethods. Thus Grace and Gauger (89) studied the technique of Millin (130) and found that excellent results could be obtained in 45 minutes with this semimicroprocedure. This method is now being studied by A.S.T.M. Committee D-5 on Coal and Coke.

Titov (200) used a semimicromethod for determination of carbon and hydrogen in coal, peat, and charcoal.

The carbon dioxide is absorbed in Ascarite, while a mixture of ground cupric oxide plus lead chromate (1 to 1) is used to absorb oxides of sulfur. A copper rod is placed in the combustion tube

near the absorption units, so that the narrower end of the tube fits almost completely into the glass tube of the first absorber containing calcium chloride. This eliminates the formation of condensate in the end of the combustion tube or in the glass tube of the absorber. In analyzing materials containing sulfur, the combustion must be conducted with a current of oxygen.

Zimmerman (211) simplified the microdetermination of carbon and hydrogen considerably. An important feature is an electrically heated furnace, by means of which the tube containing the sample can be heated little by little automatically. The combustion can be carried out not only with solid and liquid but also with gases which are measured before entering the heated chamber. Pregl's procedure is modified further by introducing a purification machine for the absorption tube which collects the moisture and carbon dioxide formed by the combustion. Pumice impregnated with silver is more suitable than silver wool because of the protection of the quartz tube. Time is saved by weighing immediately after the automatic combustion. About 13 samples can be analyzed in a 8-hour day.

Tunnicliff et al. (203) made many improvements suggested by microanalysis in macrodetermination of carbon and hydrogen, using a dual unit furnace. Two satisfactory determinations of both carbon and hydrogen can be made in 100 minutes or two extremely precise determinations in 5 hours.

Sulfur. Strambi (195) reviewed the Eschka, Carius, Foerster and Probst, Parr, Seuthe, Grote and Krekler, and Gawrilenko methods of determining sulfur and described a modified Eschka method.

A mixture of 1 gram of sample with 0.8 gram of Eschka mixture and 0.2 gram of sucrose is burned in a platinum boat in a calorimetric bomb under 30 atmospheres of oxygen in the presence of 10 ml. of 10% sodium carbonate. The products of the combustion are dissolved in water, sodium carbonate solution is added, and after acidification with hydrochloric acid, the sulfur is determined as usual. The improved method gives higher values with better agreement.

Barton and Tampa (15) have studied the determination of sulfur forms as well as total sulfur.

To determine total sulfur they (a) heat a sample for approximately 1 hour at 750° C. in a stream of oxygen and absorb the products of combustion in 3% hydrogen peroxide acidified with hydrochloric acid and (b) fuse the ash from (a) with sodium carbonate, leach with water, combine the solutions, remove silica and R$_2$O$_3$ and, finally, soluble sulfur as barium sulfate. To determine sulfate and pyrite sulfur they leach 1 gram of coal 1 hour with 1 to 1 hydrochloric acid, dilute to 250 ml., and use a 100-ml. portion for determination of iron; a 100-ml. portion is used for sulfate sulfur. R$_2$O$_3$ is removed and, finally, soluble sulfur is determined as barium sulfate. To the part of the sample not dissolved in 1 to 1 hydrochloric acid they add concentrated nitric acid and boil slowly 1 hour. Iron is determined by titration with titanium chloride and the percentage of pyritic sulfur is calculated therefrom. The remainder of the sample which did not dissolve in hydrochloric and nitric acids is ashed, fused with sodium carbonate, silica and R$_2$O$_3$ are removed, and sulfur is determined as barium sulfate. No sulfide sulfur was found in coal, but a method applicable to semicoke consists in absorbing hydrogen sulfide formed by action of hydrochloric acid in cadmium acetate and determining the precipitated cadmium sulfide iodometrically.

Complete Ultimate Analysis. Belcher and Spooner (17) give a rapid method for the ultimate analysis of coal.

Carbon, hydrogen, sulfur, and chlorine are determined simultaneously in 60 minutes by use of a simple apparatus and a tube that requires no packing. The coal, 0.5 gram, is burned in a rapid stream of oxygen at 1350° C. The sulfur dioxide and chlorine are absorbed in a spiral of silver gauze, the water in Anhydrone, and the carbon dioxide in soda asbestos. The silver sulfate is removed from the spiral by solution in hot water, and the silver chloride by solution in ammonia. Loss in weight of the silver after each treatment gives the amounts of sulfate and chloride, respectively. The results of this method were in good agreement with those from conventional methods for coals ranging from anthracite to high-volatile steam coals.

Edwards and Vahrman (61) modified the Belcher and Spooner method for the determination of carbon and hydrogen. The

absorption tubes were weighed full before and after absorption, rendering unnecessary the sweeping out of the tubes with air after each determination. Comparative determinations by this method and the method given in British Standard 1016 (1942) indicate that the new method is satisfactory for carbon, hydrogen, and sulfur. The chlorine determinations show poor agreement between the two methods, particularly for fuels containing less than 0.1% chlorine.

PLASTIC BEHAVIOR ON CARBONIZATION

The rheological behavior of coking coals on heating is becoming of increasing importance in the carbonization industries because the reserves of ideal coals for this purpose are rapidly being depleted. In order to evaluate the behavior of coals in the coke oven from simple tests, numerous procedures have been suggested but no one method has achieved general acceptance either in the industry or among fuel technologists in general.

Free Swelling Index. Mott (131) describes the British standard swelling test which employs a crucible of special dimensions with a lid, a leveled coal surface, and unidirectional heating by a gas flame at a fixed rate. The swelling of the resulting coke buttons is indicated by comparison with standard outlines numbered from 1 to 9. A similar method known as the free-swelling index is in use in this country (11). This test is helpful in selecting coals for combustion on certain types of equipment but does not distinguish between dangerous and nondangerous coals in the coke oven. Selvig and Ode have discussed this problem (172, 173). The free-swelling index is not a measure of the amount of expansion or contraction that takes place during carbonization in coke ovens and is not recommended for that purpose. A method is described for obtaining the free-swelling index of coals whose coke buttons do not conform to any of the standard profiles. The index is useful in estimating the caking behavior of bituminous coals in fuel beds.

Determination of Expansion and Carbonizing Pressure. The problem of determining whether oven damage may result from certain coals has been given much consideration by the coke, gas, and coal chemical industries. Summaries of the analytical methods published prior to the period covered in this review are given by the U. S. Bureau of Mines (29). The different methods for measuring plastic and swelling properties of bituminous coking coals were classified according to general test principles employed, and virtually all published descriptions of apparatus and procedure are summarized. Test data by different classes of test methods are evaluated.

The Mineral Industries Experiment Station of The Pennsylvania State College has published a comprehensive bulletin (142) which includes the design of a small movable wall oven for measuring volume changes and pressure developed during carbonization, as well as a discussion of the theory of the process and a bibliography of 53 references. Additional information on this subject is given by Lowry (122).

Seven suggested methods described in detail by the American Society for Testing Materials (7), include the Davis and Gieseler plastometers, four movable wall slot ovens heated from two sides, and one sole-heated oven.

Naugle et al. (135) constructed a 5-inch oven, electrically heated from both sides to investigate expansion pressures on a small scale. The results obtained were compared with the results from the large Bureau of Mines ovens and the authors conclude that correlation with the behavior of a coal in a commercial oven cannot be obtained, "mainly because the difficulties of controlling the many variables prevented the attainment of satisfactory duplicability and nice discrimination between coals or blends having different pressure characteristics."

This would seem to dispose of the suggestions that the behavior of a coal in a coke oven can be predicted from swelling pressure studies on samples of, say, 10 to 50 pounds. However, there is at present no agreement among technologists that such testing must

be made on large samples, nor that test results from large scale ovens will always predict the behavior in a commercial oven with the desired accuracy. The conclusion must be reached that the answer to this problem has not yet been attained.

Agglutination Tests. Blayden et al. (*21*) suggest that existing agglutination tests are suitable for coals of low coking properties but require addition of too much sand for highly coking coals. They suggest the use of magnesium trisilicate as a diluent. The carbonization of the coal-inert mixture was carried out as follows:

The coal sample, crushed to pass 72 B.S. sieve, was mixed with the required proportion of inert material by means of a spatula, placed in a stoppered wide-necked bottle of about 500-ml. capacity, and then rotated. Fifty grams of this mixture were placed in a Vitreosil dish (85 mm. inside diameter, 40 mm. deep, and of 200-ml. capacity) and covered by a loosely fitting Vitreosil lid. The dish was then placed on a Nichrome wire stand in a muffle furnace, previously heated to 925° C. and containing charcoal. A thermocouple (sheathed) was inserted between the bottom of the dish and the muffle floor. The muffle was closed and the dish allowed to remain until the thermocouple registered 925° C. (approximately 7 minutes). The dish was then removed and cooled in a desiccator. For determination of the microstrength of the coke, 2 grams, graded between 14 and 25 B.S. sieves, were broken down under standard conditions in a special ball mill and the percentage remaining on a 72 B.S. sieve was determined.

The results, shown graphically, suggest that surface wetting phenomena are concerned in coke formation. In the plastic state the coal undergoing carbonization probably consists of two types of colloidal materials: rigid "carbon" crystallites of colloidal dimensions formed from the humins and other thermally unstable molecules present in the original coal, or smaller amounts of a viscous, continuous phase of the thermally stable, coking coal bitumen. As carbonization progresses, the discontinuous phases increase in amount at the expense of the continuous; the adsorption of the latter on the surface of the former is an underlying cause of the final formation of a coherent coke. The admixture of colloidal inert material with the coal reduces the relative amounts of free bitumen molecules at corresponding temperatures, until, if enough is added, there is not enough to wet the surfaces of the dispersed phase to the degree necessary for the production of a coherent coke. Differences between inert materials are probably due to differences in the nature and extent of the accessible surface of these substances; their wettability may also play a part. Results of agglutination tests with magnesium trisilicate are given for 36 coals. The method is not applicable to coals of small agglutinating properties, but is believed to be valuable as a guide to the correct choice of carbonizing conditions and proper blend of coal to obtain a coke of optimum properties. The method is too elaborate for routine testing.

MISCELLANEOUS TESTS

Determination of coke strength was studied by Asbach and Brosse (*13*). Simek (*185*) developed an evaluation of the strength of coal, coke, and birquets of solid fuels from experimental results and theoretical considerations of the relations between energy input, the decrease of grain size, and the increase of surface of the test material undergoing tumbler and similar tests.

Schulte (*165*) describes the contruction and use of a vessel essentially hourglass S-shaped, with ground-glass stoppers in top and bottom compartments and a wide-bore stopcock at the constriction to facilitate separations in float and sink analysis of coal.

Grimmendahl (*91*) determines the zinc content of various coking and run-of-mine coals by ignition of the samples at 600° C. and determining the zinc as zinc pyrophosphate.

Hock (*102*) explains the theoretical principles involved in quantitative petrographic analysis of coal with the help of integration tables.

To obtain complete information on the identity, quantity, and distribution of mineral matter in coal, optical, chemical, and x-ray study is required (*134*). The application of x-ray technique is discussed and indicated with reference to certain float-and-sink fractions. Kaolinite is the chief mineral constituent in the lightest fractions examined. X-ray technique is comparatively easy, does not require elaborate equipment, and is recommended as particularly useful for identifying minerals of submicroscopic size.

Alimarin (*2*) has developed methods for the determination of germanium in ashes of coal and other industrial wastes.

Riber (*152*) discusses the ash and moisture content as well as the heating value of dry peat. Moisture is best determined by drying at 105° to 110° C. for 6 to 12 hours. For the ash determination, the peat is heated for 0.5 hour to 600° to 650° C. (this temperature is low enough so that the calcium carbonate is not decomposed); or the peat is ignited at a temperature of at least 800° C., with splitting off of carbon dioxide until constant weight is reached.

GASEOUS FUELS

Much of the attention in the analysis and testing of fuel gases has been focused on three lines: a scrutiny of the precision of the time-honored methods of complete analysis, investigations into the determination of total sulfur and sulfur compounds, and the application of new physical methods in gas analysis.

CONVENTIONAL COMPLETE ANALYSIS

The conventional methods of complete analysis have been under the scrutiny of Subcommittee VII of A.S.T.M. Committee D-3 on Gaseous Fuels ever since its inception in 1935. Shepherd prepared standard samples of a carbureted water-gas type at the National Bureau of Standards and submitted them to 24 laboratories in various parts of the country (*178*). The sample was largely hydrogen and carbon monoxide but also contained carbon dioxide, methane, ethylene, nitrogen, and ethane, with traces of oxygen, propylene, and propane. Similarly, a sample of the natural gas type containing chiefly methane, ethane, and propane with small amounts of nitrogen and carbon dioxide and a trace of unsaturated hydrocarbons, was prepared and submitted to 30 laboratories (*179*). In both cases the data from the different laboratories are presented in distribution plots for each component. There was some variation in methods and in apparatus used by the different laboratories, and the samples were also analyzed by the mass spectrometer. The check on the analytical data was made by comparing calculated with determined specific gravities and calorific values of the samples.

In general the precision of the individual determinations, except in the case of carbon dioxide, was not within the generally accepted limits. One may conclude from these careful studies that there is a real need for standardization

Carbon Monoxide. Shepherd (*180*) made a study of the determination of small amounts of carbon monoxide by ten different methods in a number of laboratories. He concluded that all methods require checking against known mixtures for calibration.

Shnidman (*182*) describes a portable apparatus for the determination of carbon monoxide in fuel gases in concentrations between 0.1% and 10 p.p.m. with the iodine pentoxide method. The accuracy is ±5 relative % for concentrations exceeding 100 p.p.m.

Berger (*19*) describes an accurate method for the determination of carbon monoxide in concentration of 0.2 to 0.5%. The method consists of absorbing carbon monoxide in cuprous sulfate–β-naphthol–sulfuric acid reagent, such as is used in usual types of apparatus for the determination of carbon monoxide in fuel and flue gases. The carbon dioxide and oxygen of the sample are removed first. With fresh reagent, 8 to 10 passes of the sample

through the bubbling pipet are enough to remove the carbon monoxide quantitatively. The method is not suitable for the analysis of samples that contain unsaturated hydrocarbons. If methane concentrations are greater than 50%, a slight error may be introduced. Accuracy and precision are within 0.05% when the concentration of carbon monoxide is 0.10% or more.

Hydrogen and Methane. Vandoni (*208*) describes an arrangement that permits a very convenient combustion of methane.

The procedure, which avoids all possibility of explosion, consists in forming in the pipet a mixture of the combustible gas and oxygen in the proportion for complete combustion and admitting this mixture a little at a time into the combustion chamber, which already contains 50 cc. of oxygen. The combustion is initiated by a platinum wire heated electrically to a vivid red (1800° C.); at this temperature the combustion is almost instantaneous. Under these conditions it is also possible to effect the combustion of wet methane without free oxygen; the traces of water react with the methane in a water-gas type of reaction to give carbon monoxide and hydrogen.

In a direct determination of hydrogen in a hydrogen-methane mixture, the catalytic effect of platinized asbestos considerably lowers the combustion temperature of the gas, but is insufficient in itself to effect the combustion of the hydrogen alone without touching the methane in the mixture, because the burning of hydrogen produces local temperatures higher than that necessary (400° C.) for the burning of methane. A modification of this method carries to the highest degree the difference in affinity of oxygen for hydrogen and methane. To this end, a slightly higher quantity of oxygen is used than that corresponding theoretically to the hydrogen. The reaction is begun at about 320° C., and the mixture is progressively heated so as to reach the maximum temperature of 400° C. only after about 1.5 hours. The reaction becomes active about 365° C. and is terminated about 380° C. In this procedure, the oxygen acts selectively on the hydrogen with none going to the methane. The absence of hydrogen in the burned gases was verified directly.

Chernyaeva (*40*) states that in the combustion of hydrogen and methane in gas analysis cupric oxide plus 1% ferric oxide plus 20 parts of white kaolin is much more active and more stable than cupric oxide alone.

Nitrogen. Shnidman and Yeaw (*184*) determine the concentration of nitric oxide in manufactured gas by passing the gas through an acidulated solution of potassium permanganate and then through an acetic acid solution of sulfanilic acid and naphthylamine. The nitric oxide in the gas is oxidized to nitrogen peroxide by the potassium permanganate solution and the nitrogen peroxide thus produced forms a red dye in the Ilosvay reagent. The depth of color is proportional to the nitric oxide content of the original gas, and its intensity can be used successfully as a colorimetric measure of this quantity by comparison with previously prepared standards. Because the Ilosvay reagent reacts not only with the nitric oxide produced by the acidulated potassium permanganate but also with any nitrogen peroxide which might have been in the gas before it reached the oxidizing scrubber, the quantity of nitrogen peroxide originally present in the gas was determined. By tests on mixtures of city gas to which measured quantities of nitric oxide had been added the factor 1.23 was derived, and should be applied to all results for nitric oxide in gas mixtures by this method. Because hydrogen sulfide will darken and destroy the pink color of the dye in the Ilosvay reagent, preliminary removal of hydrogen sulfide from the gas is necessary. The method in its present form is not considered suitable for the analysis of mixtures which contain much more than 1 or 2 p.p.m. of nitric oxide.

The method of Dudden (*56*) for the determination of small amounts of nitric oxide depends on the quantitative conversion of the nitric oxide in coal gas to nitrogen peroxide by oxidation at the anode of an electrolytic cell. The nitrogen peroxide is made to react with Griess reagent. The color developed is due to one half of the nitric oxide in the gas, and it is unnecessary to standardize the conditions and use an empirical factor. The apparatus which was developed for the test can be used as a recorder if combined with a photoelectric matching unit.

Chopin (*43*) claims that the Dumas method of determining free nitrogen in a gas can be used by passing the gas over hot cupric oxide and adsorbing the carbon dioxide in caustic alkali and then passing the unabsorbed gases through another heated tube containing cupric oxide. It is also possible to absorb the nitrogen by passing the gas over hot magnesium and recovering the nitrogen from the resulting nitride.

Oxygen. Shaw (*175*) proposed a method of determining low concentrations of oxygen in gas which consists in shaking a sample of the gas in a special flask containing ferrous hydroxide, freshly precipitated by sodium hydroxide from an acidic solution of Mohr's salt which has previously been thoroughly purged of oxygen. After shaking, the mixture is acidified and the ferric iron determined colorimetrically by thiocyanate method. Satisfactory results are obtained in the absence of volatile bases, hydrogen sulfide, hydrogen cyanide, and certain unsaturated organic compounds. All except the unsaturated organic compounds can be removed by scrubbing with acid and alkali.

The unsaturated organic compounds can be withdrawn by evacuation just before adding the acid.

Klauer et al. (*112*) used a physical method for determining oxygen in gas mixtures. Advantage is taken of the fact that a wire which is in a nonhomogeneous magnetic field undergoes a cooling when a paramagnetic gas surrounds it. When a substance in a nonhomogeneous magnetic field differs in its susceptibility from its surroundings, Maxwell energy forces are exerted on it which seek to move it to a region of greater or less energy flux density according to whether its susceptibility is greater or less than that of its surroundings. A gas sample brought to a high temperature by the heating wire is exposed to these forces and is driven out of the field, since it is diamagnetic toward the colder surroundings. The resulting gas flow cools the wire. According to the Curie law, the volume susceptibility of oxygen is proportional to the square of the absolute temperature. Measurement is made by a Wheatstone bridge. The hot wire is heated by means of a high frequency alternating current because the heating and magnetic effects interfere with each other if direct current is used. The Oersted type magnet used has a 2-mm. air gap and a field strength of approximately 7500 oersteds.

Ostermeier (*140*) determines oxygen in manufactured gases that contain sufficient hydrogen to convert the oxygen to water by burning the dry gas on a noble metal catalyst heated to 220° to 250° C. The resultant water is caused to react with magnesium nitride at 100° C., forming ammonia which is absorbed in 0.05 N acid. The volume of acid used is determined by titration. One milliliter of 0.05 N acid equals 2.4 mg. of oxygen or 1.68 ml. at 0° C., 760 mm., dry.

Stone and Shavinski (*194*) find that acetic acid solutions containing chromium chloride are excellent for absorbing oxygen in gas analysis. To prepare the reagent, sufficient $CrCl_3.xH_2O$ is taken to form the desired volume of 2 M solution, dissolved in 2 M acetic acid without heating, and made up to volume with 2 M acetic acid. The solution is forced by pressure through 0.1% mercury-zinc amalgam into the absorption pipet.

Roberts and Levin (*154*) describe a method for determining oxygen in concentrations of 0.001 to 5%.

The gas is passed over copper wetted with ammonia–ammonium chloride solution to give a mixture of cuprous and cupric oxides. The oxides are dissolved in the ammonia–ammonium chloride solution and then reduced by copper to cuprous ion. The total copper is then determined iodometrically as a measure of the oxygen in the sample. Sulfur dioxide, hydrogen sulfide, and RSH are removed by bubbling the gas through silver nitrate solution and absorption on potassium hydroxide pellets.

Szabo (*199*) proposed the following procedure for determining oxygen in gases.

With pipets add 3 ml. of a 32.5% pure sodium hydroxide solution and 3 ml. of a 40% manganese sulfate pentahydrate solution to the sample of the gas in a glass-stoppered flask. Rotate the

contents of the flask to promote oxygen absorption. Wait 12 to 30 minutes, run in 5 ml. of concentrated sulfuric acid, and shake. Then mix with 20 ml. of 0.02 N oxalic acid solution which has 1.8 N sulfuric acid as preservative. Heat to about 40° C. and titrate the excess oxalic acid with potassium permanganate.

Leithe (117) found the following procedure to be an improvement over previous procedures used.

Into a dry Bunsen buret of about 120-ml. capacity, allow the gas to flow until a slight overpressure of the gas is produced in the buret and allow this to escape into the air through a vessel containing a little water, but without allowing water to enter the buret. Pour out the water and replace it with about 1 ml. of a 1% solution of the foam and wetting agent called Nekal BX. Force this into the gas buret without allowing any air to enter. Similarly introduce 18 ml. of a reagent prepared by dissolving 35 grams of sodium hydroxide plus 115 grams of Rochelle salt plus 3.5 grams of potassium iodide in water to make 1 liter. Release the excess pressure, rinse out the vessel which was used for introducing the above-mentioned solutions, and replace with 6 ml. of a solution containing 100 grams of manganese chloride per liter. The gas volume is now 25 ml. less than that of the entire buret. Shake vigorously for 5 minutes with 2 to 3 shakes per second. Then introduce 5 ml. of 18 N sulfuric acid, transfer the liquid to a small titration flask, and rinse out the buret with two 10-ml. portions of water. Titrate with 0.01 N sodium thiosulfate to a starch end point. Excellent results were obtained in mixtures containing 0.13 to 1.23% oxygen by volume.

Sulfur. The sulfur problem facing gas chemists is twofold. One concerns the determination of the total sulfur in the gaseous fuels, and the other relates to the identification of organic sulfur compounds and their quantitative determination. The old so-called "referee's method" of determining total sulfur involving burning of a sample and recovery of sulfur as barium sulfate is widely used but has many disadvantages. As a result other methods are proposed from time to time.

Thus Il'inskaya and Kontorovich (104) burn the gas in a furnace, absorb the sulfur dioxide in neutral 3% hydrogen peroxide, resulting in the oxidation to sulfate, and measure the electric conductance of the solution or titration with 0.01 N sodium hydroxide. In gas mixtures with known contents of carbon disulfide or thiophene results were quantitative at a rate of flow of 300 liters per hour and combustion at 700° to 800° C.; under these conditions, presence of nitrogen in the gas does not interfere, as no oxides of nitrogen are formed. Below 700° C. and at too high rates of flow, combustion is incomplete; above 800° C. results are high. The combustion takes 30 minutes as against hours required by the gravimetric method.

Field and Oldach (65) convert the organic sulfur compounds in the gas to hydrogen sulfide.

The gas is passed with an excess of hydrogen over 6 ml. of 14- to 20-mesh specially prepared alumina in quartz tubes of 10-mm. inside diameter. When the alumina is at 900° C. all carbonyl sulfide, carbon disulfide, methanethiol, methyl thiocyanate, and sulfur dioxide are completely changed to hydrogen sulfide, which can be absorbed by a suitable scrubbing agent, such as sodium hydroxide solution. If oils and tars collect in the scrubber, the scrubbing solution can be treated with acid, the resulting hydrogen sulfide collected, and the process repeated. The presence of aqueous vapor is helpful but not necessary; humidification of the gas is unnecessary.

Riesz and Wohlberg (153) report a tentative method for the determination of ethyl mercaptan, thiophene, carbon disulfide and carbonyl sulfide in gas based on work with hydrogen streams containing these components.

Total sulfur is first determined by burning the gas with purified air and analyzing the combustion products for sulfur oxides. The sulfur content of the gas stream is then determined after passage through each of the following absorption trains: (1) cadmium chloride reagent, (2) cadmium chloride reagent, 95% sulfuric acid and 1 N sodium carbonate solution, (3) cadmium chloride reagent, 95% sulfuric acid, N sodium carbonate solution, and piperidine-chlorobenzene reagent, or (4) cadmium chloride reagent, 95% sulfuric acid, 1 N sodium carbonate solution, and alcoholic potassium hydroxide. The reduction in total sulfur caused

by (1) is equivalent to the mercaptan content of the gas. The sulfur determined after (1) minus that after (2) is the thiophene content of the gas. The sulfur determined after (2) minus that after (3) is the carbon disulfide and carbonyl sulfide content of the gas. The proportion of carbon disulfide and carbonyl sulfide absorbed in the piperidine-chlorobenzene reagent or the alcoholic potassium hydroxide is resolved colorimetrically.

The Railroad Commission of Texas (5) devised a procedure for determining hydrogen sulfide and mercaptan content of natural gas which consists in absorbing the gases in certain chemical solutions and titrating the solutions for the amount of sulfur present.

Slightly acidified cadmium sulfate solution is used to absorb the hydrogen sulfide and a 0.025 N solution of silver nitrate for the mercaptan gas from the hydrogen sulfide scrubber bottle. The absorber is of the Schott type with a Jena fritted-glass disk extending down inside the bottle. Approximate pore diameters are 100 to 120 microns. The cadmium sulfide is titrated with thiosulfate solution. The silver mercaptide is converted to the sodium mercaptide by the addition of a known volume of 0.025 N sodium chloride solution and the excess of the latter is titrated with a standard silver nitrate solution.

Blohm and Riesenfeld (22) determine carbon dioxide and hydrogen sulfide in natural gas by passing it first through an absorber containing a measured volume of standard barium hydrogen solution plus phenolphthalein and then into an absorber containing a measured volume of standard iodine solution plus starch indicator. The phenolphthalein color will gradually disappear on the formation of barium carbonate and the starch iodide will disappear on the oxidation of hydrogen sulfide. Each absorber is connected with a buret containing standard solution, so that the progress of the reaction can be seen at all times.

MacHattie and McNiven (125) describe an apparatus for determining organic sulfur compounds in manufactured gas. The sulfur compounds are believed to consist of mercaptans, thiophene, carbon disulfide, and carbonyl sulfide. The mercaptans can be determined directly by absorption and analysis of the absorbing solution. The others are best determined indirectly by the use of suitable selective absorbents combined with the estimation of the residual sulfur content by burning the gas and absorbing the sulfur oxides formed. The apparatus described is for the simultaneous determination of the known organic sulfur compounds in coal gas and carbureted water gas at Toronto. Selective absorbents are: for sulfur oxides 1% hydrogen peroxide, for mercaptans calcium chloride, for thiophene concentrated sulfuric acid followed by sodium carbonate solution; carbon disulfide and oxysulfides are unaffected by these reagents. Carbon disulfide is removed by passing the gas countercurrent through an oil scrubber with standard grade kerosene as the scrubbing medium. Thiophene is completely absorbed at the scrubbing rates used to remove carbon disulfide.

Hakewill and Rueck (93) propose the following tentative procedures for the determination of individual organic sulfur compounds in gas.

The amounts of hydrogen sulfide, RSH, thiophene, carbon disulfide, carbonyl sulfide, and miscellaneous organic sulfur compounds in a gas are determined by passing the gas through three trains. The first train determines total sulfur and consists of an air combustion furnace followed by a sodium bicarbonate absorption bottle. The sodium sulfite is oxidized to sodium sulfate with bromine, and the sulfate is precipitated with barium chloride. The second train has a cadmium chloride absorber for hydrogen sulfide and RSH and a sulfuric acid absorber for thiophene ahead of the furnace. The third train has in addition to the second train an alcoholic potassium hydroxide absorber for carbon disulfide and carbonyl sulfide ahead of the furnace. The cadmium chloride from train 2 is analyzed iodometrically for total sulfur. The cadmium chloride from train 3 is treated with 0.3% hydrochloric acid to separate cadmium mercaptides from cadmium sulfide; the cadmium sulfide is then determined iodometrically. Carbon disulfide and carbonyl sulfide are determined by iodometric titration of the alcoholic potassium hydroxide absorber in train three and solving two simultaneous equations. The thiophene is obtained by difference.

Compounds such as hydrogen sulfide, carbonyl sulfide, meth-anethiol, ethanethiol, methyl sulfide, carbon disulfide, and thiophene can be determined by a method based on differences in solvency in an inert solvent (63). The analysis of purified manufactured gas and coke-oven gas has given satisfactory results, but the accuracy and reliability have not been tested with gases of known composition. The quantity of the gas which contains as much solute as 1 mole of a liquid in equilibrium with it is a function of the solvency of the solute in this liquid. A No. 30 white oil can be used as the stripping liquid. The total sulfur content of the exit gases is determined by converting all the sulfur to hydrogen sulfide by means of alumina and hydrogen at 900° C. A stepwise curve shows when the sulfur content of the gas changes abruptly and it is characteristic of each specific sulfur compound; the magnitude of the change is a measure of the concentration of that compound.

In gas that contains no oxygen but may contain hydrogen, nitrogen, carbon monoxide, methane, methylene, and as much as 2% carbon dioxide, very small amounts of hydrogen sulfide can be detected and determined within 10% of the truth (64).

The hydrogen sulfide is absorbed in 6% sodium hydroxide solution and black bismuth sulfide is formed by adding a reagent prepared from 42.8 grams of bismuth nitrate in 3 liters of acetic acid and diluted with 15 liters of water, or yellow cadmium sulfide is formed by adding a solution prepared from 44 grams of uranyl nitrate heptahydrate plus 31.4 grams of cadmium acetate plus 20 liters of water plus 4 liters of acetic acid. The bismuth reagent is the more sensitive and the concentration of bismuth sulfide in the suspension can be measured in a spectrophotometer. If this instrument is not available, the concentration can be determined by the cadmium reagent, and visual comparison with a Saybolt standard universal chromometer. The method is useful in the study of catalyst poisons. A sample of 0.1 cubic foot of a gas containing only 0.011 gram of hydrogen sulfide can be analyzed satisfactorily.

Lyubich (124) determines sulfur dioxide in gases by passing a sample of the gas through an absorption bulb charged with a measured quantity of 0.1 N potassium permanganate to which are added 50 ml. of an iodine-starch solution (10 ml. of a 10% potassium iodide solution plus 25 ml. of a 0.5% starch per 1 liter of water).

MISCELLANEOUS DETERMINATIONS

Water Vapor. van den Berghe (23) found in the determination of moisture in coke-oven gas with calcium chloride that the calcium chloride should be completely dry and that the capacity of anhydrous calcium chloride from various sources for absorbing small amounts of water varies considerably and should be checked by passing the gas from the absorber tube over phosphorus pentoxide. When suitable anhydrous calcium chloride and the proper technique are used, accurate results can be secured for the water content of coke-oven gas.

Pipparelli and Simonetti (145) show that in the determination of moisture in gases by the use of magnesium nitride an error can be caused by the formation of magnesium hydroxide. This can be prevented if the reaction tube is kept at 100° C. The presence of small amounts of carbon dioxide in the gas does not interfere, but when larger quantities of carbon dioxide and water are present, ammonium carbonate is formed, part of which remains in the reaction tube.

Doladugin et al. (52) developed a method for the determining of moisture in gases based on the reaction between calcium carbide and water with the formation of calcium hydroxide and acetylene. The completeness of the absorption of the water by calcium carbide was determined by test for acetylene with the Illosva reagent. One hundred liters of gas were passed through three U-tubes filled with the calcium carbide and dry nitrogen and the gain in weight was measured.

Knublauch (113) finds that the usual methods for determining

moisture by means of hygroscopic materials do not give satisfactory results with manufactured gas.

A new method is proposed in which a gas sample is taken in a dry, 4- to 8-liter bottle provided with a tightly fitting stopper, stopcocks for inlet and outlet, an oil manometer, and a thermometer. The gas sample is allowed to come to room temperature and the pressure adjusted to atmospheric. The bottle is then shaken to break a thin-walled ampoule containing 2 to 3 ml. of water, and the maximum rise in pressure due to saturation with moisture is noted on the oil manometer. This reading is converted to millimeters of mercury and subtracted from the vapor pressure of water at the temperature. The resultant pressure is that of the water vapor at the given temperature in the gas sample; this figure divided by the vapor pressure of water at the given temperature gives the percentage saturation of the gas sample.

Grandval (90) determines the moisture content of hot unpurified gases such as producer or flue gases.

A quartz sampling tube is inserted into the hot gas main or flue and the gas sample is withdrawn through a 100- to 400-ml. buret provided with stopcocks at either end; the buret may be calibrated like an Orsat buret. This buret is placed in a boiling water bath during the sampling procedure, and the gas is aspirated at a fairly rapid rate. If necessary the sampling line is heated to avoid condensation. After the stopcocks are closed, the buret is transferred to a water bath at about room temperature. A small amount of water is introduced into the buret by momentarily opening the lower stopcock, and the buret is then shaken. This is repeated several times and the lower stopcock is then opened while the buret is held vertically. The buret is then positioned so that the distance from the level of the water bath to the level of the water in the buret is equal to the pressure in water column of the gas sampled. The shrinkage in gas volume (equals water admitted to the buret) is then read, and expressed as a percentage of buret volume. The original percentage volume of moisture in the gas as sampled is then calculated by multiplying this percentage contraction by a factor, A_t, corresponding to the cooling bath temperature; values of this factor for temperatures between 8° and 30° C. are given in a table. If the buret is not calibrated, values for the contraction can be secured by weighing the buret.

Ammonia. Accaries (1) claims a shortening of the time for the usual method for the determination of ammonia in a gas and a better accuracy can be obtained by the use of methyl red as an indicator. The amount of gas handled is 100 liters in 1 hour; the solutions used 0.005 N sulfuric acid for scrubbing, 0.05 N sodium hydroxide for titration.

Benzene. Schulte (166) increases the accuracy of the standard German method for the determination of benzene and light oils in coke-oven gases through the addition of a tube containing activated carbon to remove the light oils from the off-gases produced on steaming the usual carbon absorbent to drive the absorbed material into the measuring buret.

Gooderham (87) in determining benzene and toluene in coal gas, carbureted water gas, etc., the benzene and toluene are first removed by passing the gas through a vessel which is surrounded by dry ice and acetone. The condensed liquid is distilled through a fractionating column having the equivalent of at least three plates and the fraction boiling between 97.6° and 126.7° C. is retained. Finally the specific gravity of the toluene fraction is determined and the percentage of toluene read from a graph or when greater accuracy is desired, the determination is made by the Manning-Shepherd method.

Hydrocyanic Acid. Shaw et al. (176) determine hydrocyanic acid in coke-oven gas.

When more than 3.25 grams of hydrocyanic acid are present in 100 cubic feet of gas, scrub it at a rate of not more than 2.0 cubic feet per hour with 20 ml. of 20% potassium hydroxide in each of two Shaw S-flasks. As a sample do not use more than 2.5 cubic feet. After the absorption, add 10 to 15 drops of $(NH_4)_2S_x$ solution. This treatment with polysulfide can sometimes be omitted when a small sample of acid gas is taken. Let stand 2 minutes; add concentrated hydrochloric acid slowly until the yellow color of the solution disappears and about 8 ml. per 100 ml. of solution in excess. Cool and evacuate until most of the air in the flask is removed. Through the adjustable vent in the funnel top of the

flask add increments of potassium bromide-bromate solution (125 grams of potassium bromide, and 25 grams of potassium bromate per liter) until about 2.0 ml. are present in excess. After 2 to 3 minutes add 1 ml. of 5% phenol solution, mix, add 4 ml. of 50% potassium iodide, and titrate with thiosulfate. In this procedure, the hydrocyanic acid is converted into alkali cyanide, the CN^- is changed to CNS^-, so that it is not changed back to volatile hydrocyanic acid on adding acid, the CNS^- is changed to $CNBr^-$, excess bromine is removed by adding phenol, and the $CNBr^-$ reacts with the 2 HI to form hydrocyanic acid, hydrobromic acid and iodine.

Tar and Oils. Scheeben (*160*) discusses the errors in the determination of tar and oil mists in coke-oven gas due to incorrect determination of water.

Pass 1200 to 1500 liters of gas through a weighed glass tube tightly packed with absorbing cotton; the increase in weight is due to water, oil, and tar mists. Add propyl alcohol and 5 grams of magnesium nitride and heat for 0.5 hour with a reflux condenser. Distill three fourths of the mixture into 20 ml. of N sulfuric acid plus 100 ml. of propyl alcohol, and back titrate the acid. The amount of sulfuric acid consumed minus sulfuric acid consumed in a blank test, multiplied by 0.05405, gives the water content.

Schultzky (*167*) determines tar and dust simultaneously in a special apparatus by separating the suspended particles by a fritted-glass filter and absorbing the tar in toluene, from which it is subsequently separated by vacuum distillation on the steam bath.

INFRARED AND MASS SPECTROMETRIC METHODS

Under the stimulus of the war considerable activity was developed in the use of infrared radiation and mass spectrometry in gas analysis. Both techniques offer great promise particularly for control purposes where large numbers of samples must be analyzed quickly. Shepherd (*181*) studied the reproducibility of results on a standard sample submitted to twenty laboratories and reports that the results were better than those obtained by chemical methods.

Brewer (*27*) and Brewer and Dibeler (*28*) outline the basic principles underlying mass-spectrometric analysis of gas mixtures.

The molecules are dissociated into all possible fragments by 50-volt ionizing electrons; the fragments of each molecular species always occur in the same abundance ratio. The relative abundance of fragments with values of m/e between 24 and 60 is tabulated for nine C_4 hydrocarbons. Four galvanometers of progressively decreasing sensitivity are used to record the contributions of the various mass numbers. To interpret the galvanometer record it is necessary to know the cracking pattern and the sensitivity of each component that might be present. The method of calculation is described and representative analyses of crude, refined, and recovered butadienes, of noncondensable gases from styrene condenser, of oil-flame fumes, of tank helium, of natural gas, and of various gas mixtures are given. For direct analysis the vapor pressure of the material should exceed 1 mm. of mercury at room temperature, but much less volatile material can be analyzed by using special methods. Stereoisomers give very similar cracking patterns and are consequently difficult to separate. An instrument that covers a range of masses up to 150 is sufficient for all hydrocarbon analyses. Duplicate determinations usually check within a few hundredths of 1%, but owing to uncertainty in all such analyses the actual accuracy of the method is, in general, unknown.

Solomon and Rubin (*189*) use the mass spectrometer for determination of such gases as oxygen, nitrogen, carbon monoxide, carbon dioxide, hydrogen methane, acetylene, methylene, butane, pentanes, and n-pentane, and predict that the time will soon come when no well equipped laboratory dealing with hydrocarbons will be without the instrument. Fairly good results can be obtained more quickly than by means of any other method of analysis, although experience is necessary to interpret the results accurately.

Hipple and associates (*99–101*) state that the mass spectroscope is useful in tracer work with stable isotopes, determination of small traces of gas in mixtures, for leakage testing, and for other determinations where chemical methods are not applicable.

Johnsen (*106*) proposes a new method of mass spectrometric analysis in which the usual pressure measurement of the sample prior to expansion is not necessary. The method utilizes a ratio of the peaks of the two components; thus errors normally associated with the pressure measurements are avoided. Similarly, temperature fluctuations and electrical fluctuations affect both components equally. An average error of ±5% appears in the analysis of benzene for small amounts of cyclobenzene, ±5 to 6% in analysis of methylcyclohexane in toluene, and ±3 to 4% for diethylbenzene in ethylbenzene. This ratio method can be applied to binary mixtures of isomers; n- and iso-, cis- and *trans*-, o- and m-, or any other isomeric binary type in which the mass spectra are sufficiently different to permit an analysis to be made. It is not easily applicable to the analysis of ternary isomeric mixtures.

Brattain and Beeck (*26*) describe two prism spectrometers that may be used in infrared analytical methods for hydrocarbon mixtures. In one the slit widths and prism settings are more readily adjustable than in the other. They are both designed for the region from 2 to 15μ, but other regions can be covered by using a material other than rock salt for prisms and windows. The source of radiation is a specially constructed Nernst glower, sealed for use in fire restricted areas. An analysis accurate to ±0.5% of the total sample can be made in 20 minutes on butane and isobutane mixtures and 1-butene and 2-butene mixtures.

Brattain (*25*) explains the method of selecting the spectral position, slit width, and concentration of sample for the routine infrared spectroscopic analysis of mixtures of hydrocarbons with the aid of specific examples of mixtures of butane and pentane; and of mixtures of 1-butene and 2-butene; of methane, ethane, ethylene, propane; and the optical system of the instrument built by the Shell Development Company for such routine analysis is diagrammed.

Luft (*123*) gives a new method of gas analysis by means of infrared absorption without spectral splitting. The principle is the same as that used by Pfund and Gemmill, though there are differences in detail. The apparatus which has high selectivity, sensitivity, and speed, is purely physical, and is applicable to complex mixtures of gases.

Coggeshall and Saier (*46*) used a Perkin-Elmer Model 12A spectrometer and a null method for measuring the thermocouple signals in the analyses of light gases.

The gas cells were 9.5 cm. long, with rock salt windows. Gas mixtures were stirred with steel diaphragms operated by electromagnets, or by gravity. Curves are shown for the absorption of gases that display pressure broadening. The absorptions of methane and carbon dioxide at constant partial pressure are increased by increasing the pressure of foreign gases, such as hydrogen, nitrogen, and oxygen, these three exerting practically the same effect. For routine analyses the total pressure of methane and other gases (hydrogen, nitrogen, oxygen or air) is adjusted to 80 cm. of mercury and the partial pressure of methane is read from a calibration curve. Flue gases containing sulfur dioxide, carbon dioxide, and carbon monoxide were analyzed for these three gases in the presence of one another, with air as the added gas. The differences between known and observed concentrations did not exceed 0.4%.

Brady (*24*) describes the optical systems of the Beckman model DU quartz spectrophotometer and of the Perkin-Elmer infrared spectrometer. Ultraviolet absorption curves of benzene and toluene and the 10 mμ absorption band of ammonia are reproduced.

Gordon and Powell (*88*) state that aromatic hydrocarbons containing 2,3,4 compounds can be analyzed by means of ultraviolet radiation with fair accuracy.

Specific Gravity and Density. A critical study of eleven commercial instruments for determining specific gravities of gases was made by the National Bureau of Standards. Fifteen test gases

of known specific gravities ranging from helium (specific gravity 0.15) to butane (specific gravity 2.06) were used in this investigation. Determinations of accuracy and reproducibility, of the effects of changes of temperature, relative humidity, and water content of the surrounding air, and of sources of error and applicable corrections were made. The instruments tested were Edwards balance, Ac-Me Junior and Senior balances, Anubis portable balance, Anubis and Ac-Me recording gravitometers, Sigma recorder, Metric indicating gravitometer, Ranarex specific gravity recorder, and portable gravity indicator and Fisher densimeter. This work by Smith, Eiseman, and Creitz (187) represents the most complete discussion of the subject available at the present time.

Karawat (110) determines the density of a gas by weighing it under pressure.

From 3 to 4 grams of the gas are weighed under 8 atmospheres' pressure in a metal sphere about 8 cm. in diameter. After the sphere has been connected to a gas thermometer or similar apparatus, the pressure, volume, and temperature are determined after the pressure is released. The method is claimed to be accurate within a few ten-thousandths of the density value.

Calorific Value. The most important development in this determination was the publication of a tentative method of test for calorific value of gaseous fuels by the water-flow calorimeter (6, 12). This presents detailed requirements of apparatus and full descriptions of test procedure with the various adjustments needed for humidity correction and humidity control, theory of calculations and corrections to be applied, calculation of total and net heating value, and a discussion of reproducibility of results. The maximum permissible difference between the results of duplicate determination of calorific value of a given sample of gas by the same observer using a single set of apparatus is 0.3%. The maximum permissible difference between results of determination of calorific value of a given sample of gas by different observers using different apparatus is 0.5%. Headlee and Hall (95) find that the total, T, and net, N, heating values of natural gas determined with a water-flow calorimeter are related by the equation

$$T - 1.072 N = 34 - 0.34 I$$

where I is the percentage of inserts. The equation was derived from data of the first six saturated normal hydrocarbons and holds for natural gas within the limits of deviation of the gas from the law of partial pressures.

A new caloriscope is described by Duchene (55) for obtaining relative calorific values of gases by burning them in a vertical copper tube and determining the linear expansion of the tube.

TAR AND THE LIGHT OILS

TAR

Coulson and Jones (49) analyzed low temperature tars and separated them into the conventional groups of compounds by extraction with ether. Neutral oils, phenols, and bases contain benzene, toluene, the xylenes, phenol, naphthalene, anthracenoid hydrocarbons, and complex resins. Anthracene homologs that were found in low temperature tar are β-methyl-, dimethyl-, trimethyl-, and tetramethyl anthracene. Dimethylnaphthacene, polymethyl phenols, 2-methyl-5-ethyl phenol and 2,3,6-trimethyl phenol were identified.

Gauger, Kinney, and Struck (81) made an investigation of water gas tar emulsions to determine the individual components of these tars, so that they might be better exploited by the industry. Flash vacuum distillation and solvent extraction methods were most satisfactory for isolating the resin-forming hydrocarbons. Styrene, indene, and their simple derivatives were identified. Hot storage induces polymerization of many of the unsaturated hydrocarbons. Storage at room temperature has little effect. Dehydration of tar emulsions by pentane may break the

emulsion but does not dissolve all the resin-forming molecules. Isopropyl alcohol is another promising solvent.

Renaudie (150) found the amount of carbon black in tars to vary with the nature of the solvent employed. Higher surface tension of the solvent tends to give lower results. Lower surface tension solvents leave in addition to the graphitic material a residue containing various asphaltic resins. A detailed method for determining insolubles is given for a number of solvents. A second method describes the determination of true carbon black (C_1) in tar or pitch by the use of filtered, nondephenolized anthracene oil using 200 ml. of anthracene oil per 10 grams of tar or 5 grams of pitch and extracting at 100° to 120° C. The filters are washed with benzene.

Mantel and Schreiber (126) determined total sulfur in tar oils and distillation residues by the following method.

Steam is superheated by being passed through a clean quartz combustion tube placed in an electric furnace, then over a boat containing the sample and a catalyst mixture, is condensed in a section of the tube kept cool with running water, and finally is passed through an absorption flask containing cadmium acetate and a second catch flask with a little of the same solution. Temperatures vary from 350° to 1100° C. depending upon whether oils or hard residues are analyzed. The catalyzing mixture is made from 6 parts by weight of calcium oxalate, pulverized and free of sulfur, 2.5 parts of calcium hydroxide, 1.0 part of ammonium molybdate, 3 parts of wood charcoal, pulverized to 2500-mesh, and 1 part of activated carbon, pulverized and free of sulfur. Samples of 1.3 grams for oil or 2.0 grams for distillate residue are so chosen that not more than 15 to 16 ml. of 0.5 N iodine solution will be needed for the titration. The absorption solution contains 50 grams of cadmium acetate and 10 ml. of glacial acetic acid per liter; 50 ml. of this solution and 200 ml. of water are placed in the absorption flask. Upon heating the sample in a current of superheated steam all the sulfur is removed as hydrogen sulfide, caught in the absorption flask as cadmium sulfide, and treated as usual for sulfur.

Schlapfer (162) discussed two methods for tar-acid determination.

The STIAG (Swiss Tar Industry A.G.) method determines tar acids by distilling the 170° to 270° C. fraction out of tar and distilling this with steam after adding dilute phosphoric acid to it, followed by titration of the distillate with 0.2 N sodium hydroxide solution. The accuracy of the method is not too good and depends on distillation time. Suggested modifications include refluxing the acidified mixture for 1 hour prior to steam distillation. The E.M.P.A. method is believed more reliable. It determines total acidity in the tar by adding 10 ml. of concentrated phosphoric acid directly to 50 ml. of tar, mixing with 150 ml. of xylene, and distilling off the xylene up to 150° C. After the distillation the aqueous layer is separated and the xylene repeatedly washed until neutral. The aqueous solution is titrated with 0.2 N sodium hydroxide solution. If necessary, chlorine is determined separately.

Suttle (196) discussed fractional distillation as an analytical tool with particular reference to the works laboratory. The distillation of the light oils was discussed and a suitable fractionating column was described. Methods which can be used in the identification of compounds boiling below 80° C. are listed.

van der Linden (119) compared the Dutch standard "thief" sampler with the Van't Sant sampler. The difference is mainly that the spring closure is below in the former and above in the latter. The importance of moving the open thief sampler downward slowly is emphasized as essential to good results. The deviation depends upon the viscosity of the tar, a rate of 10 cm. per second is considered the maximum, and errors up to 30% can be made even at that speed. The Van't Sant sampler gives the better results.

BENZENE, TOLUENE, AND XYLENE

Florentin (76) described a method for the rapid and accurate determination of the three aromatic hydrocarbons that may be present in factory air. The method is based on the fact that the absorption spectra of benzene, toluene, and xylene are different in the ultraviolet. Their coefficients of absorption show striking

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differences, especially at 2475, 2575, and 2650 Å. These data and the fact that Beer's law applies to mixtures of these three hydrocarbons make it possible to establish three equations with three unknowns which can be solved. The apparatus consists of an H lamp to provide a continuous spectrum of constant intensity in the ultraviolet, a quartz condenser, a double absorption cell, a quartz monochromator, a photoelectric cell, and an electric amplifier. It was found that absolute alcohol cooled to −10° C. retains nearly all the benzene contained in the air that is passed through 10 cm. of it. This solution forms the test sample for spectrophotometric examination.

Mel'nikov and Senilov (127) determined the amount of benzene vapor in air by a method based on the continuous measurement of the electric conductance of a liquid which is passed through a Wright suction flask. The purified air sample is heated in a tube furnace and passed through the suction flask. The electric conductance is determined from the galvanometer readings. A detailed description of the apparatus is given and the results of the experiments are discussed.

Fuoss and Mead (78) analyzed two-component systems.

Light from a globar is directed along two paths to a pair of opposing thermocouples connected in series to a galvanometer. Rock salt cells containing compound A are placed in each beam and the galvanometer is set to zero by a shunt resistance across one thermocouple. When the compound is changed in one cell by adding compound B, a galvanometer deflection is produced if the total transmission of A differs from that for mixtures of A and B. This method requires no prism or other dispersion device to separate different wave lengths of light. Curves are shown for benzene and carbon tetrachloride, benzene and toluene, and other two-component systems where galvanometer currents rises from 1 to 1.5 amperes as the B component increases from zero to 100 volume %.

Traynard (202) applied Raman spectra to the quantitative analysis of binary mixtures of benzene and toluene. Each plate is calibrated by the method of varying slit width. The background of the spectrum is raised to its threshold value by a preliminary exposure to continuous radiation and the intensity of the background is subtracted from that of the Raman lines.

Dolin (53) described a method for the determination of benzene in the liquid or vapor phase by its conversion to m-dinitrobenzene at room temperature and the formation of a color complex with butanone, sodium, hydroxide, and the m-dinitrobenzene in alcohol which is fairly stable upon the addition of acetic acid. Toluene, xylene, and ethylbenzene similarly treated do not form such stable complexes. No color is produced with aliphatic hydrocarbons or alcohols, ketones, and esters. The method can be used for both qualitative and quantitative analysis.

Hardy (94) shows that commercial benzenes are best analyzed by fractionating and determination of density. The chief impurities are carbon disulfide, thiophene, and indene. Carbon disulfide is tested for with aniline, according to Hoffman, and the hydrogen sulfide formed is detected by lead acetate test paper, or in alkaline solution with sodium nitroprusside.

Baernstein (14) analyzed mixtures of benzene and toluene by oxidizing the latter to dinitrobenzoic acid, which gives no color under the prescribed conditions.

The nitration is effected in a small U-tube filled with beads by means of 2.0 ml. of fuming nitric acid for a sample of 10 to 100 micrograms. The tube and its contents are heated to 90° C. for 15 minutes. If benzene alone is to be determined, one drop of chromic acid solution is added and mixed by bubbling air through the solution. The tube is returned to the oil bath and heated at 90° C. for another 15 minutes, then transferred to a 60-ml. glass-stoppered bottle with the aid of three 2.0-ml. portions of water. It is cooled in ice water, and neutralized carefully with 70% potassium hydroxide solution until the dichromate changes to chromate, yellow green. After addition of 10 ml. of butanone and vigorous shaking, it is placed in a water bath at 60° C. and shaken frequently during 5 to 10 minutes. Then it is transferred to a jacketed buret kept at about 60° C. while removing the beads in a funnel tube containing a wire so that the beads do not choke the funnel tube. The layers are allowed to separate in the buret, the lower aqueous layer carefully drawn, and the nitrated sample

in butanone drawn into a 25-ml. glass-stoppered measuring cylinder. Then 10 ml. of 70% potassium hydroxide solution are added and shaken 2 minutes. The colored layer is allowed to separate, transferred to the cell of the photometer, and the color measured within 5 minutes.

Chernyaeva (41) described a physicochemical method for determining benzene in coke-oven or illuminating gas and reported on the adsorption capacities of charcoals with respect to benzene, on the losses of benzene during steam distillation, on the effect of the gas velocity on the completeness of the adsorption of benzene, and on the effect of hydrogen sulfide and moisture on the activity of the charcoals. The losses of benzene during steam distillation depend on the amount of steam and on the construction of the apparatus. Not more than 5 grams of steam per minute are recommended. Steam distillation is necessary for the regeneration of the charcoal. The optimum velocity of gas is 200 to 300 liters per hour. The presence of hydrogen sulfide decreases the accuracy and lengthens the time required for the determination.

van der Linden (118) used a method for the rapid determination of benzene in city gas in which the benzene is absorbed from a few liters of gas with Tetralin, and the benzene content of the gas was calculated from the change in weight, the temperature, and the vapor pressure of the Tetralin. Standardized tests with air saturated with benzene showed deviations from standard values between + 0.6 and −2.8%.

Glasgow (86) purified and determined the freezing points of 31 hydrocarbons, including benzene, toluene, and the three xylenes.

Geist (83) determined the viscosities and densities of pure hydrocarbons and gives values for benzene, toluene, and the xylenes.

Schnurmann (164) measured the ultraviolet absorption spectra of solutions containing a number of aromatic hydrocarbons between about 2400 and 2700 Å. The hydrocarbons were benzene, toluene, ethyl phenol, propyl phenol, synthetic xylenes, styrene, chrysene, and a chrysene fraction from catalytically cracked petroleum. Alkyl substituents enhanced the weak benzene band at 2786 Å.; the enhancement decreases in the following order: toluene, ethyl phenol, and propyl phenol. Despite the difficulties of obtaining the spectra and interpreting the results, an analysis can be achieved with reasonable results as to the order of magnitude of the percentage composition.

Campbell (36) described a method for determining the composition of mixtures of benzene, ethyl alcohol, and carbon tetrachloride from the refractive index and density of the solution.

Bishop and Wallace (20) developed a method for determining small quantities of benzene in cyclohexane by measuring the heat of reaction with nitric acid of definite concentration.

French and Claxton (77) estimated small quantities of sulfur in benzene by the use of a wick chamber burner through which air is drawn and which enables 24 ml. or more of benzene to be burned in 3 hours. As little as 0.01% of sulfur can be determined accurately.

Reichel (148) determined the composition of a xylene mixture by the use of the following method:

While cooling with ice, carefully mix 5 ml. of the xylene sample with 20 ml. of glacial acetic acid and 40 ml. of nitric acid (density 1.5) and finally 40 ml. of concentrated sulfuric acid. After nitrating for 0.5 hour in the cold, heat on the water bath for 1 to 2 hours, cool in ice water, and dilute with 450 ml. of cold water. After another 0.5 hour filter with the aid of suction and wash thoroughly with cold water. Under a reflux condenser treat the mass of crystals with 100 ml. of acetone on the steam bath, cool with ice water, and filter off the precipitate at 15° C. Dry at 95° C. and weigh the trinitro-m-xylene. The weight of the crystals plus 0.6 gram for each 100 ml. of acetone used multiplied by 10.2 gives the corresponding per cent content of m-xylene. Next evaporate the acetone mother liquor to dryness, add 100 ml. of ethyl alcohol, and boil a short time under a reflux condenser. Cool, filter at

15° C., and boil dry this new crop of crystals at 95° C. before weighing. To the weight of trinitro-p-xylene now obtained add 0.2 gram to allow for solution in 100 ml. of alcohol. If m-xylene is present, subtract 0.6 gram per 100 ml. of acetone and multiply the resulting number by 14.3 to give the per cent content of p-xylene.

CRESOLS

Robertson (155) made quantitative analyses of isomeric cresol and cresol-phenol mixtures by the use of a 3-mm. grating spectrograph with a 70-cm. quartz absorption cell and a 2.5-kv.-amp. H discharge tube as light source.

Absorption spectrograms were made for pure o-, m-, and p-cresols (I, II, III), and phenol (IV) and for the vapor in equilibrium with synthetic mixtures of known composition at 25° C. Working curves were prepared from the measured density differences between centers of strongest bands of (I) and (III) 2744 and 2930 Å., respectively, and the background, and can be used for mixtures containing up to 50% of (I) or 70% of (III). Because of its low intensity the band 2779 Å. for (II) was compared with the band 2694 for (I) and had to be corrected for a low intensity band (III) in the same region. Working curves for (IV) were prepared by using the sharp band 2636.7 Å. for values up to 40% and 2750.3 Å. for values up to 5%. Concentration as low as 0.3% of (IV) in cresol mixtures can be determined. Concentrations above 50% of (I), 70% of (III), or 40% of (IV) can be analyzed by addition of known amounts of the m- or other isomer to decrease the relative concentrations or by the use of an additional short cell. The mean deviation between the known compositions of these mixtures and the values determined from the working curves for (I), (II), and (III), is less than 2% and for (IV) 3%.

PHENOL

Chopin (42) determined phenol in tar or distillates gravimetrically.

Weigh out 8 to 9 grams of sample carefully, transfer from the weighing dish to a separatory funnel by means of 50 ml. of carbon tetrachloride, and a volume of 10% aqueous solution of sodium hydroxide equal to twice that of the carbon tetrachloride. Agitate the mixture for 30 to 40 minutes. Decant off the solution during 15 minutes. Wash the aqueous solutions of phenates with 50 ml. more carbon tetrachloride. Decompose the phenates in the aqueous solution by adding 30 to 40 ml. of 6 N hydrochloric acid. To extract the phenol from this mixture add 20 ml. of carbon tetrachloride or chloroform, agitate 3 minutes, and withdraw the carbon tetrachloride layer through a glass filtering crucible. Repeat this operation 5 times. Distill with a thermometer in the flask until the phenols show a tendency to come over. Eliminate moisture by adding 10 ml. of benzene and distill again. Cool and weigh the residual phenols.
A volumetric procedure is the following: Take 7 or 8 ml. of an oil of known density which has been dried over sodium sulfate. Put the separatory funnel in a water bath or on a stove at 40° C., so that the oil will be fluid. Add 10% aqueous sodium hydroxide in volume exactly equal to that of the sample. Add 30 ml. of well dried carbon tetrachloride, shake for at least 30 minutes, and allow to stand until the two liquids are well separated. Draw off the bottom layer and repeat the treatment with fresh carbon tetrachloride but agitating only 15 minutes. Draw off the bottom layer and repeat for the third time. Read the volume of carbon tetrachloride and that of the aqueous solution before and after the treatments. The carbon tetrachloride is the best solvent for the paraffins and is least soluble in the sodium hydroxide.

Paris and Vial (141) described a new physicochemical method for the analysis of phenols. It is a turbidity-temperature method for determination of (a) phenol in mixtures with o-cresol, (b) phenol in mixtures with isomeric cresols, and (c) cresols in binary mixtures with xylenes. In (b) the error is less than 0.5% if the content of cresol is less than 50%. In (c) the errors are 1 to 2%, 2 to 3%, 3 to 4% when cresol content are 0 to 40%, 40 to 70%, 70 to 100%, respectively. In (a) and (b) turbidity-temperature ranges between 40° and 95° C., in (c) between 48° and 85° C.

Ioffe and Sokolova (105) determined small quantities of monophenols in the presence of polyphenols and quinone by the oxidation of the latter with hydrogen peroxide.

Treat 10 ml. of the test solution containing about 0.0002 mole per liter with 1 ml. of 25 to 30% hydrogen peroxide and 5 ml. of 20% ammonium hydroxide. After 2 to 3 hours remove the excess hydrogen peroxide by adding manganese dioxide, neutralize the filtrate with hydrochloric acid, treat with diazosulfanilic acid solution in the presence of sodium carbonate and ammonium hydroxide at 0° to 5° C., and measure the color in a photometer.

NAPHTHALENE

Love and Padgett (121) determined aromatics and naphthalene in complex hydrocarbon mixtures containing olefins by a relatively simple and rapid method. Naphtha containing up to 40% olefins can be analyzed.

Interfering olefins, if present, are removed by bromination, followed by steam distillation to separate the bromides from unchanged hydrocarbons. The olefin-free distillate is then separated into fractions of the desired boiling ranges by distillation and the selected fractions are extracted with 93 to 94% sulfuric acid to a constant, n. The aromatic content of the fractions is calculated from the n upon acid extraction and the naphthalene content of the fractions is calculated from the n after acid extraction and the average of the n's of pure paraffins and pure naphthenes in the same boiling range as the fraction. The method is accurate to about 0.3% on aromatics and about 1% on naphthenes. The method is limited in that it will not reveal unsaturated naphthenes, it will not distinguish between the C_8 aromatics, between naphthenes of the same boiling range, or between the various dimethylcyclohexanes.

Cerveny and Hinckley (38) described a rapid method applicable to all mixtures of naphthalene, Tetralin, and Decalin which gives values within ±1% of the truth. Only two measurements are required, the heat of reaction of the sample with nitrating acid and the temperature at which the first crystals of naphthalene appear upon cooling a sample while stirring (cloud-point temperature). The four-component system (naphthalene–tetralin–cis-Decalin–$trans$-Decalin) behaves like a two-component system with respect to the acid heat test, one component being naphthalene-Tetralin and the other cis-Decalin–$trans$-Decalin. In the cloud test the four-component system also behaves like a two-component system, the components being naphthalene and Tetralin-Decalin. Thus Decalin is determined by the acid heat test, naphthalene by the cloud test, and Tetralin by difference.

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FERROUS METALLURGY

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PRACTICAL advances in ferrous analytical chemistry from the beginning of World War II to the present are the culmination of earlier fundamental research in many branches of science. A description of these advances is of necessity restricted largely to published information, but an attempt has been made to include here methods and procedures that have been reported since the beginning of 1942 for determining either the presence or amount of an element or compound in a ferrous matrix. Practical advances in ferrous analysis have been facilitated by development of new tools for and by the chemist, by the growing recognition by management of the value of research in pointing the way to better utilization of raw materials in the production of improved products, and by the urgency of wartime needs for better and more rapid analytical methods.

NEW TOOLS

The quality of work produced by a skilled craftsman is a reflection of his knowledge, ingenuity, and skill in using the tools at his disposal. Improved tools may be the means for securing better and more economical workmanship. New or improved tools—i.e., instruments and apparatus—have served as a stimulus and have become a valuable adjunct to the more conventional and classical methods of the analytical chemist in industry; and he has adopted many of them for research and to lighten the burden of routine work handled by his laboratory.

The spectrograph was used routinely for ferrous analysis in this country prior to 1942, but the period since then has witnessed a very rapid growth in its use and in the manufacture of instruments and accessories designed for industrial requirements. At the present time emission, absorption, and x-ray spectra are utilized for both qualitative and quantitative ferrous analysis in research and as a guide to manufacturing operations. Published descriptions of a number of these installations and applications of the spectrochemical method include papers on laboratory arrangement (*62*); precision of the method (*170*); routine (*25, 83, 103*) and special (*26, 30, 32, 33, 55, 86, 93, 135, 157*) techniques; types of sample used (*45, 48, 64, 75, 95, 125, 147, 188*); and requirements for equipment (*63*). The literature on spectrochemical analysis has been indexed from 1920 to 1945 (*143*). Two books on this subject were recently published (*72, 140*) as well as a booklet listing standard samples available for spectrochemical analysis (*29*). Gillis (*58*) reviewed the current status of quantitative spectroscopy.

The foregoing references pertain mainly to the conventional spectrograph which utilizes a photographic emulsion for recording the emission spectrum of the element. A more recent development has been the direct-reading spectrometer, two general types of which may now be procured. One is a modification of the conventional spectrograph with electron-multiplier phototubes substituted for the photographic emulsion as a means for recording and measuring the intensity of the desired spectral line from the excited element (*19, 74, 76, 168*). The other utilizes x-rays as a means for exciting the secondary radiation ("fluorescence") of the impurities in the iron matrix. This secondary radiation is monochromated and the intensity of the lines of the different elements measured by means of a Geiger-Müller counter (*2, 50*). Both types of direct-reading spectrometers represent methods and apparatus not available 6 years ago but now in daily use by chemists for research and production control.

The principal technical limitation of the spectrograph at present is its inability to analyze for such nonmetals as carbon and sulfur or to analyze for all alloying elements in all concentra-

tion ranges. The ultimate place each type will make for itself remains to be determined from a longer period of use. At present, it appears that the various types complement rather than duplicate each other.

A much older spectrochemical method in terms of its utilization in ferrous analysis involves use of the absorption spectrum, mainly in the visible region, as the basis for quantitative analysis. Utilization of this method has been facilitated by development of photoelectric spectrophotometers, some of them automatically recording, filter photometers, and by discovery of new reagents which can be utilized as a basis for color reactions or as a medium by which a given element may be separated from interfering elements. The status of this method of analysis was reviewed recently (*113*) and books by Sandell (*138*) and Welcher (*177*) contain valuable information for those who have unusual analytical problems or who wish to use the absorption method for analysis. Furman, Bricker, and McDuffie (*53*) utilized the mercury cathode separation as a starting point for colorimetric and polarographic determination of traces of metals. This method appears to have likely application in ferrous analysis.

X-ray diffraction as a means for quantitative analysis has come into increased use in recent years. Its utilization has been stimulated by development of direct-recording x-ray spectrometers and publication of x-ray diffraction data (*1, 49, 61, 99, 131*). There is at present a very serious need for publication of more x-ray diffraction data on industrially important compounds.

Potentiometric methods have important applications in ferrous analysis, as do electrolytic methods. Apparatus and procedures for utilization of these techniques were summarized in recent reviews (*20, 52, 106*). Probably the best source of information on practical new methods of ferrous analysis, other than current technical articles, is the book revised and published every three years by the American Society for Testing Materials (*28*).

Any discussion of apparatus developments would be incomplete without brief mention of some of the less spectacular but, nevertheless, important pieces of equipment that have become commonplace within recent years. These include high temperature combustion furnaces which, with their accessories, have made the present-day rapid carbon and sulfur analyses possible on virtually all ferrous materials; improved gas analysis units; a new, rapid type of direct reading balance; and better laboratories—better from the standpoint of both arrangement and of cleanliness and ventilation. Continued progress in this direction will prove necessary if the demand for improved accuracy and for analysis of ferrous metals for trace constituents continues. Some applications of new methods and apparatus to specific analyses are considered in subsequent paragraphs.

NEW METHODS

The identification of metals and of their constituents is common in most laboratories and may become necessary at any stage in a manufacturing operation or may be required as a guide in determining what quantitative methods are applicable to a given sample. The spectrograph was evaluated for qualitative work by Standen (*155*). Norman and Johnson (*124*) give data on the limits of detection of phosphorus, titanium, and zirconium in various materials with the spectrograph. Tuttle and Nahstoll (*165*) designed a mobile laboratory that can be used for qualitative work. Bryan and Nahstoll (*17*) describe a technique for the microspectroscopy of metals. In general, for the detection of metallic impurities, spectrochemical methods are unequaled. Frequently, however, simple spot tests such as those described by

Kirtchik (97) and others (4, 161, 162, 181) may be used to good advantage. These tests are economical and nondestructive.

Aluminum. Aluminum may be added to steel either as a deoxidizer or as an alloying element. Hence it may occur in amounts from traces up to quantities in excess of 1% and may be in a matrix containing several alloying elements in addition to iron. The spectrograph may be used for its determination (147, 154) either with a solid specimen or by use of a solution obtained by dissolving the sample in acid. Improved mercury cathode apparatus for separating aluminum from iron has been described (88, 129) and also a method for its utilization (126). Craft and Makepeace (34) extract iron from the aluminum in acid solution with isopropyl ether and then determine the aluminum colorimetrically with ammonium aurintricarboxylate. Ammonium benzoate was recommended by Smales (148) for separating aluminum from iron. Wilson (186) found that by using this reagent in conjunction with thioglycolic acid to form a stable soluble iron complex, aluminum could be precipitated and determined in the presence of iron. Smith and Cagle (149) utilized the ferrous-bipyridine complex to determine aluminum in ores in the presence of iron. Weissler and White (176) utilized the reaction of Ponta-chrome Blue Black R(Colour Index 202) with aluminum to form a solution which fluoresces at 636 to 700 millimicrons. The intensity of the fluorescence was measured and correlated with the aluminum content of the steel. Kuskova (102) investigated various colorimetric procedures for determing aluminum in steel. The foregoing methods may be used in analyzing for either the acid-soluble or total aluminum content of steel.

Arsenic. Arsenic is not frequently a constituent of domestic ferrous metals and few new procedures for its determination in these materials appear to have been developed recently. Smith and Wilcox (151) describe the dyes Amaranth, Brilliant Ponceaux 5R, and Naphthol Blue Black as improved indicators for the titration of arsenous trichloride in acid solution. Davies and Key (36) determine arsenic and copper in pyrites by means of an internal electrolysis method.

Boron. Boron in small amounts has come into relatively widespread use in steel within recent years. The reaction of quinalizarin with boron in concentrated sulfuric acid has been made the basis for color methods (136, 173). The reaction of curcumin with boron also has been utilized as the basis for a color method (28). White, Weissler, and Busker (184) utilized the reaction of benzoin in 85% ethyl alcohol in devising a fluorometric procedure. In this method the boron must first be separated from iron by distillation as methyl borate. Corliss and Scribner (31) developed a spectrochemical method for determining this element in steel. These methods are all designed for determining boron in small quantities.

Carbon. Carbon is a constituent of all steels. Recent investigations of methods for determining carbon have been made as a result of the need for determining accurately the small amounts present in some types of steel. Detailed descriptions of apparatus and procedures for determining carbon in the range of 0.01% with an accuracy in the range of ±0.0003% have been published (66, 119–121, 156, 189). These all involve some form of low pressure combustion. The conventional combustion method also has been modified for determination of small amounts of carbon (42, 122). A spectrochemical method for determining carbon has been described (54).

Cerium. Cerium has been utilized as an addition to certain types of iron. Westwood and Mayer (183) determined this element colorimetrically after converting the iron to ferrocyanide and extracting the cerium from the solution as the cerous salt of 8-hydroxyquinoline at a pH in the range of 9.9 to 10.5 with a chloroform-acetone solution. They found a preliminary separation with the mercury cathode necessary for highly alloyed irons. The method was not recommended for irons containing more than 0.3% vanadium.

Chromium. Chromium may be present in steel in amounts ranging from traces to more than 50% of the sample. For determination of traces, colorimetric methods have been developed, such as those described by Baker (9) and Ege and Silverman (40) utilizing the reactions of chromium with 1,8-dihydroxy-naphthalene-3,6-disulfonate and with an alcoholic solution of diphenyl carbazide containing phthalic anhydride. For somewhat larger amounts, color methods involving measurements of the intensity of the oxidized chromium have been utilized (35, 39, 146, 152). Vaughan and Whalley (169) devised a micromethod for analyzing steels and were able to make complete analyses (for 13 elements) on 80-mg. samples. Potentiometric methods for the determination of chromium have been described (28, 142, 145), as have a number of spectrochemical methods (32, 75, 147).

Cobalt. Cobalt was separated from iron with tribasic sodium phosphate by Young and Hall (192), and then determined electrolytically. Methods for the colorimetric determination of this element as the thiocyanate in an amyl alcohol–ether mixture are also described (68). Bayliss and Pickering (11) describe use of the thiocyanate complex as a basis for separating cobalt from interfering elements. They found a 35% solution of amyl alcohol in ether to be the best solvent for the complex. Uri (166) defines the conditions for determining cobalt as the thiocyanate complex in an ethyl alcohol–water solution. Procedures for analysis of high temperature alloys for cobalt include potentiometric titration with potassium ferricyanide solution (9, 84). Putsche and Malooly (128) utilize the thiocyanate complex in an acetone solution as a basis for the colorimetric determination of cobalt in stainless steels. Sharova, Chufarov, and Shnee (144) studied the mechanism for separating cobalt and nickel with sodium hypochlorite. Samanta and Sen (137) used pyridine in place of zinc oxide for separating iron and cobalt. Tananaev and Silnitschenko (160) precipitate iron in a weakly acid solution with sodium fluoride before determining cobalt. Young, Pinkney, and Dick (193) describe use of nitroso R salt as basis for a colorimetric method for determining small amounts of cobalt. Waldbauer and Ward (171) utilized a chloroform solution of the cobalt salt of nitroso-β-naphthol as basis for a photometric method for determining cobalt. Bagshawe and Hobson (7) made a critical comparison of potentiometric methods for titrating the cobaltous ion with potassium ferricyanide in ammoniacal citrate solution with the nitroso R salt colorimetric method. They found the potentiometric method suitable for general routine analyses but inferior to the color method. Chirnside and Cluley (24) describe an accurate method for analysis of low expansion alloys for cobalt, nickel, iron, and manganese. They investigated the properties of the iron-cobalt dimethylglyoxime complex also.

Columbium and tantalum. Columbium may be separated from titanium and both elements determined in steel according to a method described by Traub (164). A 10% solution of hexamethylenetetramine is used in place of hydrogen sulfide in making separations. The procedure is also suggested for determining zirconium. Harpham (71) described a gravimetric method for the determination of columbium and tantalum in tungsten-bearing heat-resistant steels. Rogers (133) outlined procedures for routine analysis of 18-8 steels for columbium and tantalum. Johnson (87) describes both gravimetric and colorimetric methods for determining columbium in stainless steel. Procedures are also given for titanium and tungsten. Malooly (111) described the colorimetric determination of columbium. Hasler's (75) spectrochemical method for analyzing stainless steels includes a procedure for columbium. Chernikhov and Goryushina (23) and Bagshawe, Elwell, and Craven (6) review the analytical properties of columbium and tantalum.

Copper. Copper may be determined colorimetrically on the basis of its reaction in tartaric acid solution with the sodium salt of diethyldithiocarbamate (85) or as the cuprammonium ion (115). Flagg and Vanas (46) investigated quinaldic acid as a precipitant in the gravimetric determination of copper. Clardy, Edwards, and Leavitt (27) were able to determine copper by precipitating it

as cuprous thiocyanate from a perchloric acid solution and titrating the thiocyanate with potassium iodate in the presence of chloroform. Usatenko and Datsenko (167) precipitate iron in acetic acid solution with sodium fluoride and titrate the copper with sodium thiosulfate. Levine and Seaman (105) describe electrolytic and colorimetric methods suitable for its determination. Castro and Pheline (22) describe a spectrochemical method for determining small amounts of copper.

Germanium. Germanium may be separated from iron by distillation as the tetrachloride, precipitated with tannin, ignited, and weighed according to a procedure described by Weissler (174).

Hydrogen. Hydrogen in ferrous metals has been the subject of much investigation but its importance still remains a matter for speculation. Methods for its determination involve heating either in vacuum or in oxygen with collection and measurement of the evolved gases. Apparatus and techniques for its determination have been described (3, 5, 158, 178).

Iron. Iron may be titrated with dichromate after reduction with silver by a procedure described by Henry and Gelbach (78). Smith and Kurtz (150) investigated liquid amalgams for use as reducers in analytical work.

Lead. Lead may be extracted from iron with a chloroform solution of dithiozone and determined colorimetrically (14) or it may be determined polarographically (67). These methods supplement gravimetric procedures (28).

Manganese. Manganese, like carbon, is universally present in iron and steel and satisfactory methods for its determination are available. Spectrochemical methods have replaced others in many laboratories where the spectrograph is used for other elements also. Few new methods for determination of manganese in steel have been described in recent years. Hillson (81) investigated the use of osmium as a catalyst in the arsenite titration of large amounts of manganese. This method was said to be suitable for determination of manganese in high grade ores. Lingane and Karplus (107) titrated the manganese ion with permanganate potentiometrically in a neutral pyrophosphate solution by a procedure that is said to be suitable for use in ores, ferroalloys, and steels. Watters and Kolthoff (172) separate manganese from vanadium, chromium, and iron with pyridine, convert the manganese to tri-dihydrogen pyrophosphatomanganate, and determine the manganese content with the polarograph.

Molybdenum. Molybdenum may be determined in microquantities in steel by the procedure of Wells and Pemberton (179) involving the color complex of molybdenum with toluene-3,4-dithiol (Dithiol) in amyl acetate solution. The method is said to be virtually specific for molybdenum in steel. Kapron and Hehman (90) develop the molybdenum-thiocyanate color complex in a solution of ethylene glycol monobutyl ether or diethylene glycol monobutyl ether and measure its intensity without extracting the molybdenum from the iron. Weissler (175) utilizes the peroxide complexes of molybdenum, titanium, and vanadium to determine these elements in the same solution by means of spectrophotometric measurements. Cass (21) investigated oxinates under various conditions for separating molybdenum, tungsten, and iron. Gregory, Foulson, and Gray (60) describe an improved gravimetric method for determining molybdenum.

Nickel. Nickel in the presence of large amounts of iron was determined by Passamaneck (127) by precipitation as the glyoxime from an ammoniacal citrate solution, solution of the precipitate in pyridine, and measurement of the intensity of the color of the pyridine solution. This method was intended for small amounts of nickel only. Mitchell and Mellon (117) studied the nickel dimethylglyoxime complex as a basis for the colorimetric determination of nickel, as did Makepeace and Craft (110). Kirtchik (96) described a method suitable for determining 0.05 to 0.30% nickel in the presence of 20 to 60% cobalt in complex alloys. Johnson and Simmons (89) investigated nioxime (1,2-cyclohexanedionedioxime) for the gravi-

metric and colorimetric determination of nickel. West and Dean (182) described a polarographic method for its determination; sodium fluoride was used as a supporting electrolyte. Evans (43) described a method for titrating small amounts of nickel with potassium cyanide.

Nitrogen. Nitrogen analyses in steel have become commonplace in recent years and steam distillation has replaced direct heating as a means for separating the nitrogen from the iron matrix (12, 28, 132). Vacuum fusion methods which are most valuable for oxygen analyses are also used for nitrogen. Brown (16) compared data obtained by the usual solution distillation method with those secured with vacuum fusion apparatus. Kempf and Neuberger (92) investigated the possibility that mechanical work such as drilling and abrasion might cause an enrichment of the nitrogen content of steel, and concluded that ordinary methods of sample preparation could be used without danger of causing nitrogen pickup. Moreau and Chaudron (118) liberated the nitrogen from steel by ionic bombardment, but this method of analyzing for nitrogen does not appear to have found general acceptance thus far.

Gotta and Seehof (59) and Newell (123) determined nitrogen by precipitating iron as the hydroxide, removing it by filtration, and nesslerizing a portion of the remaining solution. Leitch and Wells (104) point out some of the errors that may occur in the filtering operation. Khrizman and Korneichuk (94) determined nitrogen in nitrided material by heating the specimens in hydrogen and absorbing the ammonia formed by reaction of hydrogen with the nitrogen in the steel. Perhaps the most difficult problem in determining nitrogen in ferrous metals is in decomposing nitrogen compounds in the iron matrix; nitrogen forms physically and chemically stable compounds with some constituents in steel.

Osmium. Osmium may be separated from iron by distillation, and determined colorimetrically by means of its reaction with thiourea according to a procedure described by Sandell (139).

Oxygen. Oxygen is most commonly determined in ferrous materials by the vacuum fusion method. Improved apparatus and techniques have been described recently for this determination (3, 37, 38).

Phosphorus. Phosphorus may be determined in steel with the spectrograph (18, 70). More common methods recently utilized are based on the yellow molybdovanadophosphoric acid (73, 80, 98, 141, 185) or the molybdenum blue (91, 152) color complexes. Both these complexes have been investigated by a number of workers and various techniques suitable for analyzing steel and ores for phosphorus described. Speight (153) and West (180) modified the usual alkali-molybdate method for use on steels containing such elements as titanium, vanadium, and zirconium. Rainbow (130) devised a micromethod in which he extracted the phosphorus from iron with isoamyl alcohol and reduced the phosphorus to the molybdenum blue complex for measurement of its color intensity in ethyl alcohol solution.

Silicon. Silicon may be determined colorimetrically in steel as the yellow silicomolybdate complex (134). This method is said to be suitable for routine use. Gentry and Sherrington (57) reduced the yellow complex to molybdenum blue with ferrous sulfate and oxalic acid and completed the determination colorimetrically. Gelatin (47, 65, 69, 159) and joiner's glue have been utilized as coagulants in speeding up the gravimetric determination of silicon. Kordon (100) converts the silicon in steel to potassium silicofluoride and titrates it with sodium hydroxide, while Mika (114) utilizes an acid solution of pyridine in a volumetric micromethod for silicon.

Sulfur. Sulfur may be determined in small quantities of metal according to a method described by Markova and Gutman (112) by ignition of the sample in hydrogen at 1300° C. The sulfur is converted to hydrogen sulfide and absorbed in p-phenylenedimethyldiamine and the sulfur content estimated colorimetrically. Heppell (79) describes a method for determining sulfur by burning

the steel in oxygen at 1300° C., absorbing the combustion products in water, and titrating the sulfur with potassium iodate using a starch indicator. Belcher and Postlethwaite (13) utilized a similar procedure but absorbed the combustion gases in a weak solution of hydrogen peroxide and titrated the sulfur with borax solution using bromocresol purple as an indicator. Hedberg and Schwartz (77) use silver nitrate as an absorbent in the combustion procedure. Wilson and Bennett (187) absorb the combustion products in potassium iodate and back titrate with sodium thiosulfate.

Ingram (82) describes a microcombustion method with which the sulfur content of steel samples as small as 10 mg. can be determined. Progress in the determination of sulfur in steels in recent years has seen the combustion method, which, as yet, is empirical, replace to a large extent the older evolution and gravimetric methods. General agreement has not been reached as to the exact conditions for combustion and filtering of combustion gases prior to absorption, but active work in progress should eventually enable a stoichiometric recovery of sulfur to be obtained. The method in its present empirical form is a valuable one from the standpoint of both its accuracy and speed for many ferrous materials.

Tin. Tin is separated by distillation and determined colorimetrically as the molybdenum blue complex by a procedure described by Baker, Martin, and Gibbs (10).

Titanium. Titanium along with vanadium and molybdenum was determined as the hydrogen peroxide complexes of these elements by Weissler (175) by measurement of their absorption at 410, 460, and 330 mμ, respectively. Milner, Proctor, and Weinberg (116) also utilized the peroxide complex as a basis for the determination of titanium. Yoe and Armstrong (190) investigated disodium-1,2-dihydroxybenzene-3,5-disulfonate for the colorimetric determination of titanium. Traub (164) found hexamethylenetetramine to be superior to hydrogen sulfide in separating iron from titanium prior to its determination. Zan'ko, Geller, and Nikitin (194) utilized a polarograph for determining titanium in iron and steel.

Tungsten. Tungsten was determined colorimetrically in steels as the tungsten–toluene-3,4-dithiol complex by Vaughan and Whalley (169). Bagshawe and Truman (8) modified this method to avoid interference from the corresponding molybdenum-dithiol complex by forming it preferentially in a cold dilute acid solution and removing it by extraction in amyl acetate. The tungsten-dithiol complex was then developed quantitatively in hot concentrated acid and extracted with amyl acetate. The method is said to be applicable to most alloy steels and for micro and semimicrosamples. Emery (41) determined tungsten colorimetrically as the thiocyanate after reducing it with titanous chloride. Gentry and Sherrington (56) used tin amalgam in hydrochloric acid solution to reduce the tungsten prior to the colorimetric determination as the thiocyanate. Johnson (87) also utilizes a color method. Fisher, Spiers, and Lisan (44) determine tungsten spectrochemically by sparking a carbon electrode impregnated with a solution containing the tungsten, which is first separated from any columbium present. Yoe and Jones (191) investigated the compound anti-1,5-di-(p-methoxyphenyl)-1-hydroxylamino-3-oximino-4-pentene as a reagent for use in place of cinchonine in analyzing for tungsten. Touhey and Redmond (163) and Furey and Cunningham (51) describe methods for the analysis of metal carbides.

Vanadium. Vanadium in steel may be determined polarographically after removal of interfering elements by methods described by Lingane and Meites (108, 109).

Zinc. Zinc was extracted from iron with a chloroform solution of dithiozone and determined colorimetrically by Bricker, Weinberg, and Proctor (15).

Zirconium. Zirconium in hydrochloric acid solution was found by Kumins (101) to react quantitatively with mandelic acid. This reaction may have merit for determining this element in ferrous materials.

SUMMARY

Developments in analytical chemistry over the past 6 years in instrumentation and in methods have been discussed. An endeavor has been made to cite apparatus and methods that are useful in solution of the everyday and special problems encountered in laboratories analyzing ferrous materials. This article, which is the first of an annual series, may have omitted mention of important apparatus or methods. It is hoped that such omissions will be brought to the attention of the editors, so that they may be included in a future article.

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NONFERROUS METALLURGY

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BECAUSE the analytical chemists serving nonferrous metallurgy use many, if not most, of the analytical procedures and techniques covered in the general and specific literature of analysis, detailed descriptions of techniques and procedures are avoided in this review. The scope of use of techniques and procedures and their application to the analysis of nonferrous metals are stressed.

Fundamentally, the most important analytical procedures in the nonferrous field are gravimetric and volumetric in nature. This is well illustrated by the fact that, for the most part, methods for the analysis of nonferrous metals presented by the American Society for Testing Materials (3) are almost wholly gravimetric or volumetric in nature. This fact should not be construed as minimizing the importance of other procedural methods, but rather as indicative of the fact that from the standpoint of demonstrable accuracy, gravimetric and volumetric methods have advantages not attainable by methods which, while not necessarily so accurate, exhibit the advantages of speed and adequate precision.

Most of the accessory methods used for purposes of speed and convenience are comparative in nature and depend for their reliability on standards evaluated by the more reliable, even if more laborious, methods of gravimetric and volumetric analysis.

During the past five years, there has been little advance in the gravimetric and volumetric methods used in the field of nonferrous metallurgy. In general, these methods closely parallel the procedures outlined in what is generally accepted as the analytical bible of nonferrous analytical chemistry, Hillebrand and Lundell's "Applied Inorganic Analysis" (15). In general the gravimetric and volumetric methods used in the nonferrous field are covered in essence by the text of Lundell and Hoffman (21). In this area of analysis, wide use is made of standard texts on quantitative analysis such as that by Kolthoff and Sandell (20). Texts such as the latter are of great value as regards fundamental theory and practice, but must be supplemented by literature which covers specific fields, as the application of certain basic or fundamental methods to the determination of elements in a specific matrix or in the presence of certain interfering ele-

ments often makes necessary the provision of specific procedures for the separation of such interfering elements prior to the measurement of the element sought by weighing or titration. In such cases, texts such as Scott's "Standard Methods of Chemical Analysis" (28) are of great value. In the same category as Scott's compendium of methods are such publications pertaining to particular or specific fields as "Analytical Methods for Aluminum Alloys" (2) or "Chemical Analysis of Aluminum" (1).

Electroanalysis has continued to be an important procedure in nonferrous analytical laboratories. However, no particularly new or novel advance has characterized the use of such procedures in the nonferrous field during the past five years.

No particularly noteworthy application of potentiometric methods has been made during the past few years, although there is a gradually increasing use of potentiometric procedures to supplant less precise and convenient procedures.

Although there has been no recent important development in the field of organic reagents as precipitants, the use of dimethylglyoxime, nitroso-β-naphthol, and many other such reagents in the nonferrous field is widespread. The increasing use of 8-hydroxyquinoline is particularly noteworthy. Nonferrous chemists are keenly aware of the possibilities involved in organic precipitants, particularly those with selectivity or specificity as to elements, and are alert to new developments in the field.

TRACE ANALYSIS

In the nonferrous field, few metallic elements are determined when they are the matrix or base metal of the alloy. General practice is to determine the concentration of certain impurities, summate the total of these, and report the difference between these and 100% as the concentration of the major or matrix metallic element. Many trace elements or those without known metallurgical effects are often not determined. However, the number of elements not determined continually grow less as metallurgical investigations reveal the specific effects of many elements, even when present in minute amounts. The determination of elements present in minute amounts has been greatly

facilitated by the development of colorimetric, spectrochemical, and polarographic procedures. Attention is called to the recent publication of Sandell's "Colorimetric Determination of Traces of Metals" (25), which is generally accepted as authoritative, helpful literature in the field of trace analysis.

The analytical chemistry of nonferrous metallurgy, as it developed, was historical in character; comparatively little actual control analysis was accomplished. During the process of production of either the metal itself or the alloy, the metal in process was not analyzed in time for modification, correction, or adjustment of composition to be made. It is true that certain step or end products were analyzed, but these were made to establish historically the result of other control procedures and to establish the quality of product. The condition arose from necessity and not from desire. The simple fact was that the traditional methods available could not be speeded up sufficiently to enable their use as practicable control procedures. The development of physicochemical methods during the past 25 or 30 years, however, offered a possible solution to the problem and, today, methods of adequate precision and speed either are available or are in process of development to enable the introduction and use of spot control procedures which must inevitably result in better quality of product and in greater economy of production costs.

Another advantage of the physicochemical methods is their much greater objectivity in contrast to the large element of subjectivity in the traditional gravimetric and volumetric procedures. Although instrumentaton and mechanization have been incorporated into the traditional or classic methods, nevertheless, over-all progress along that line has not served to stem the increasing use of the newer physical procedures.

In 1938–39, there appeared Böttger's excellent treatise entitled "Physikalische Methoden der analytischen Chemie" (5) although no English translation of this work has been published, it has had a stimulating influence on the development of methods of analysis in the nonferrous field. R. H. Müller's article on "Instrumental Methods of Analysis" (23) published in the ANALYTICAL EDITION of INDUSTRIAL AND ENGINEERING CHEMISTRY in 1941, which has been supplemented by several additional papers in the same journal by the same author, gave great impetus to the objectivization and speeding up of analytical work in the service of nonferrous metallurgy. Also worthy of note is Gibb's excellent volume published in 1942 (13).

COLORIMETRIC METHODS

Much specific use of colorimetric methods has been made by nonferrous chemists. However, such methods, as yet, have not attained the status of general use. Indicative of progress in the more general use of colorimetric procedures in the nonferrous field is the intensive attention being paid to this type of procedure by the nonferrous division of Committee E-3, American Society for Testing Materials. Certain methods and procedures along these lines appear in recent editions of the A.S.T.M. volume on "Methods of Chemical Analysis of Metals" (3). The availability of photoelectric instrumentation has given great impetus toward the more general adoption of colorimetric or photometric methods as they are referred to increasingly. Volume I of Snell's "Colorimetric Methods of Analysis" (30) is a widely used source book, as is Yoe's "Photometric Chemical Analysis" (32). Sandell's book on trace elements (25) also is attaining wide acceptance.

While photometric methods present many interesting possibilities, it is probable that such methods are used in nonferrous analytical laboratories to only a limited extent and for very specific purposes. Closely allied to colorimetric or photometric methods are those called spectrophotometric procedures. In the nonferrous field, spectrophotometry is used mainly in the investigation and setting up of colorimetric or photometric procedures, wherein the spectrophotometer is supplanted or replaced by the photoelectric colorimeter, usually of the filter type.

The most popular physicochemical methods are those commonly referred to as spectrographic but more definitely as spectrochemical. In general, such procedures have found wide acceptance throughout the whole field of nonferrous metal analysis, but, perhaps, are more widely used for the analysis of magnesium- and aluminum-base metals than for the analysis of other nonferrous materials. Although there has been no such generally accepted compilation of spectrochemical methods as the A.S.T.M. methods, which are largely in the traditional or classic vein of gravimetric or volumetric analysis, the fundamental principles and techniques are well covered in two texts—Brode's "Chemical Spectroscopy" (7) and Sawyer's "Experimental Spectroscopy" (27). The adaptation of spectrographic procedures to the analysis of particular base metals is covered in many separate publications, such as ANALYTICAL CHEMISTRY and the Journal of the Optical Society of America. In the case of some metals such as aluminum, methods specific for that metal are available from a producer. Sources of information along spectrochemical lines, particularly of a nonferrous nature, are given in the bibliography appended to this review. Considerable information of great value is also available from manufacturers of apparatus and equipment.

In general, the methods employed are adaptations or modifications of the so-called internal standard type. The use of visual comparison methods still persists but is gradually being abandoned. This has been caused mainly by the better adaptation of internal standard spectrochemical methods to the mass or speed production of analytical data.

Spectrochemical methods are comparative in nature and depend for reliability and validity of results obtained by their use upon the availability of reliable standards upon which to base working curves, adjustment of instruments, and control of analytical operations. The status and availability of spectrographic standards for use in the nonferrous field are well covered in a report by Brode and Scribner. Many standards for use in the analysis of specific nonferrous alloys or metals are available from metal or alloy producers. Most standards used in the nonferrous field are secondary standards, for few primary standards have been prepared.

The advantages of spectrochemical methods for the mass and speed production of analytical data were attained only by a drastic and stringent establishment and maintenance of appropriate conditions and practices. However, experience revealed that the photographic variables were the most difficult to control. Mainly in an effort to overcome such difficulties, cooperation between spectrochemists and instrument manufacturers led to what is probably the most significant development in the field of nonferrous analytical chemistry—the so-called direct reading spectrographs. Two such types of instrumentation are currently serving in the field of nonferrous metallurgy, though further developments are apparently in the offing.

In essence, these instruments replace the photographic plate or film with photoelectric receivers positioned to receive radiation on any desired wave length. These receivers are built around multiplier phototubes, the output of which is used to charge condensers. Available instruments vary in the method of measuring the charge on the condensers, but regardless of the method of measurement, the charge on the condenser is a direct and calculable function of the radiation which has impinged on the multiplier tube. The measurement may be registered as a count of impulses and the tape or other counting device may be directly calibrated so that the measurement may be read in percentage of element spectrally excited.

In one nonferrous industry, laboratories engaged in routine metal analysis produce analytical determinations using traditional methods at the rate of about five per man-hour. This rate per man-hour is arrived at by dividing the total determinations reported per day, first by the number of hours in the work day, and then by the number of productive chemical workers. Labo-

ratories doing work on similar samples by conventional spectrographic methods show a production of about twenty-five determinations per man-hour. When the work is done on direct reading spectrographs, the output reaches as high as eighty per man-hour. This speed of production is not obtained with any sacrifice of precision or accuracy. As a matter of fact, careful statistical studies show that the standard errors of direct spectrographic results are no greater, and often are less, than the standard errors of results obtained routinely by the use of conventional chemical methods. In general, ordinary spectrographic methods are acceptable for concentrations of less than about 4%; however, cases can be cited when this limit of concentration is exceeded. In the case of direct reading spectrographs, concentrations up to 13% are being determined satisfactorily and adequately.

One very important use of the spectrograph in the nonferrous field is for qualitative purposes. Many nonferrous analytical laboratories routinely check samples of current production for the presence of unexpected elements. Another prevalent use of the spectrograph is the identification of the alloy type of samples of metals and alloys. This identification of alloy types or qualitative compositions is more satisfactory and definitive than the use of chemical spot tests. Experienced spectrographic workers become expert in their qualitative work and their results are rightly referred to as semiquantitative. One widespread practice is to report qualitative results on a decimal scale, thus listing elements as 10 to 100%, 1 to 10%, 0.1 to 1.0%, 0.01 to 0.10%, 0.001 to 0.01%, and less than 0.001%

The spectrograph is also widely used for the sampling and identification of scrap. Such procedures have been of great value in the postwar period when vast quantities of scrapped nonferrous material were in process of recovery. Much of the nonferrous metal used commercially is of secondary origin, and its composition is often controlled by spectrographic procedures.

An interesting variant of spectrochemical analysis of the usual type is the combination of direct reading spectrographic techniques with the flame excitation of spectra which was proposed by Lundegårdh in Norway. The apparatus is known as the flame photometer. Two such instruments are at present available commercially and are receiving increasing acceptance by nonferrous analytical laboratories. In flame photometer procedures, the sample, after solution, is atomized into a gas flame. The radiation from this flame is fed into the apparatus, wherein, by the use of either filters or a refracting prism, radiation on particular wave lengths is allowed to impinge on a photosensitive surface. By measurement of the element current produced and comparison with similar radiation from known standards, the concentration of the emitting element can be calculated. Although the method has proved to be of value mainly in the case of alkali and alkaline earth metals, many other elements are also sufficiently spectrally sensitive to be determined. In the nonferrous field, only threshold experience has been had with this instrument, but it apparently offers great promise.

Analyses by x-ray spectrography, x-ray diffraction, mass spectrography, and radiometry have not, as yet, become particularly important in the nonferrous field, and for the purposes of this review are recognized only by name. It is to be expected that some or all of them will become increasingly useful, particularly in specific applications, but it is doubtful if for some time to come they will challenge in popular use the more widely used methods already described.

Chromatographic methods do not, as yet, seem to offer much promise to the nonferrous analytical chemist as a major procedure.

Microanalysis and chemical microscopy are, of course, used to some extent in the field of nonferrous metals, but have proved to be useful only in isolated specific cases. There is little in the literature to indicate that nonferrous analytical chemists have contributed much to the development of these techniques which

have proved to be of great value in other fields. The spot testing techniques of Feigl (12) are rather widely used in nonferrous qualitative work.

POLAROGRAPHIC PROCEDURES

There remains one other type of analytical procedure that offers considerable promise in the field of nonferrous analysis — namely, polarographic procedures. While the techniques of polarographic analysis stemming from the work of Heyrovský have been the subject of many publications, the American nonferrous analytical chemist has based most of his work on the book by Kolthoff and Lingane (18). Attention is called to Kolthoff's paper (16), which outlines workable procedures for applying polarographic techniques to the analysis of aluminum alloys. This particular paper is cited because it shows that polarographic procedures are applicable to a nonferrous sample. It is doubtful that polarographic procedures can compete on a routine basis with other methods now in wide use in nonferrous analytical laboratories, particularly from the standpoint of economy of laboratory manpower. However, the time seems to be rapidly approaching when polarographic equipment will be considered essential and standard in a modern nonferrous laboratory.

The following publications are specifically useful for the identification of published material on nonferrous analysis: *Chemical Abstracts*, AMERICAN CHEMICAL SOCIETY, Washington 6, D. C., published since 1907; and *Metallurgical Abstracts*, The Institute of Metals, London, England, published since 1934.

CONCLUSIONS

During the past few years nonferrous analytical laboratories have been going through a process of evolution from a state wherein the analytical data were largely historical in character to a state where most data are provided in sufficient time actually to serve as a control on the composition of metal in process. This change has been particularly marked during and since World War II. It has been characterized by a change from the more subjective methods of traditional analytical chemical methods of a few years ago to the increasingly objective methods of today. However, all this has been accomplished by the intelligent use of the traditional or classic procedures to produce adequate standards upon which to base the comparative methods which are being used to an increasing extent.

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PETROLEUM

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THE trend of development and progress in analysis is a good index of development and progress in the petroleum industry generally, as these have paralleled each other closely. This review includes the period from just before our entry into World War II until September 1948. So much progress in this field and in chemistry generally has been stimulated by requirements imposed by wartime products and processes, that reaching that far into the past seemed necessary to give a good picture of the advances that have been made.

As in other industrial fields, the increased acceptance of relatively newer tools of analysis is quickly manifested. In this category are microchemistry, refractometry, polarography, chromatography, radiation chemistry including ultraviolet, infrared, and Raman, emission spectrometry, x-ray, mass spectrometry, and refinements in high and low temperature analytical distillation.

CRUDE OIL

Horne (*103*) determined salt in crude oil by dissolving the sample in xylene, adding a destabilizer to prevent emulsification, extracting the salts with water, and titrating with silver nitrate. Neilson (*171*) used a somewhat similar procedure, employing phenol to break emulsions, and removing interfering sulfur compounds by preliminary treatment with cadmium salts. Mukherjee (*169*), using alumina, applied a chromatographic method in which fluorescence of solutions of the adsorbate was used to differentiate crude oils.

GAS

Ludeman (*142*) described a method for determining the dissolution temperature of aniline and butanes and Francis (*71*) applied dissolution temperature in o-nitrotoluene to determine the composition of binary mixtures of iso- and n-butane. Ferber (*67*) used alumina and active carbon at low temperatures in a study of adsorption and desorption for analysis of gaseous hydrocarbon mixtures, in which olefins were preliminarily hydrogenated, as the method is for paraffin hydrocarbons. Turner (*225*) employed a column of charcoal for adsorption and by heating separated the constituents in the zones up to, and including, hexane.

Miller (*164*) analyzed mixtures of propane, isobutane, and n-butane for plant control by a simple weathering test conducted in a centrifuge tube. Liljenstein (*132*) used a combination absorption-weathering test in which the volume of residue was the basis for determining isobutane and heavier and pentanes and heavier; it is used for plant control purposes. Hamblen (*90*) used a weathering test for plant control, in determining propane contamination in butane. Tooke (*223*), in plant control, used a time-temperature distillation curve to analyze n-butane for isobutane, propane, and pentane. Solomon (*213*) described a hydrometer for determining the density of small samples of liquefied butane-isobutane mixtures. Echols (*62*) analyzed three-component light hydrocarbon mixtures by isothermal distillation.

Eberl (*61*) employed silver sulfate in dilute sulfuric acid to determine ethylene in butane, claiming no butane absorption. Cuneo (*50*), in determining butadiene in mixtures with saturated and other unsaturated hydrocarbons, used a mercuric nitrate reagent to obtain a volumetric determination of mono-olefins plus diolefins. Francis (*72*) employed mercuric sulfate in dilute sulfuric acid to determine ethylene and claimed the reagent was applicable to determination of total olefins. Mapstone (*156*) studied numerous reagents for determining ethylene and total olefin in gas and concluded that mercuric sulfate reagent was best. Stanerson (*214*) collected gaseous sample in cold chloroform, titrated this solution with bromine in glacial acetic acid, and concluded that the method is comparable in results with hydrogenation but simpler to conduct. Houtman (*104*) employed aqueous hydrochloric acid at room temperature to determine isobutene in mixtures with other unsaturated and saturated hydrocarbon gases; only isobutane reacted to form tert-butyl chloride. Cyclopentadiene was determined colorimetrically by Uhrig (*228*) after prior condensation with benzaldehyde to form its highly colored fulvene.

In determining ethylacetylene and vinylacetylene in C_4 hydrocarbon gases, Thomas (*221*) employed silver nitrate titration, hydrogenation, bromine titration, and maleic anhydride absorption. Robey (*194*) improved the hydrogenation procedure of McMillan by correcting for nonideal behavior of gaseous hydrocarbons. Corner (*46*) employed selective hydrogenation involving a nickel-kieselguhr catalyst partially deactivated with mercury to determine cyclopropane in the presence of propylene. Ransley (*183*) described a micromethod for analyzing gaseous mixtures, applicable to 0.1 ml. of sample, in which the volume is kept constant and the individual constituents are determined from changes in pressure on reaction with specified reagents. Pyke (*181*), employing the apparatus of Blacet and Leighton in microdeterminations of gaseous olefins, used a paste containing

mercuric acetate, boron trifluoride, ethyl etherate, and ethylene glycol on a platinum loop absorbent holder.

A novel technique was described by Gooderham (83), who analyzed mixtures of gases by determining volumes in a series of burets containing reagents, soap films being the meters. The method is stated to be rapid and accurate but requires 1 liter of sample. Savelli (197) studied various low temperature distillation apparatus and methods employed in analysis of hydrocarbon gases, as well as dew point and reagent methods for determining composition of gaseous mixtures. Reporting on cooperative work on analysis of a sample consisting of non-hydrocarbon and hydrocarbon gases, Shepherd (208) concluded that need for standardization is apparent.

Uhrig (229) determined traces of oxygen in hydrocarbon gases by a modification of the MacHattie procedure in which oxygen reacts with copper wetted with an ammoniacal solution. Trace quantities of basic nitrogen in hydrocarbon gases were determined by Donn (57) by collection in substantially nonaqueous standard sulfuric acid in acetone. Balis (13) describes a microcombustion procedure for the simultaneous determination of carbon, hydrogen, and chlorine in gaseous compounds; the method is also employed to determine traces of incompletely burned material in hot exhaust gases.

Powell (178) employed ultraviolet absorption to determine cyclopentadiene and methylcyclopentadiene. Brady (29) used infrared absorption for the determination of impurities in butadiene and claimed that the butadiene values by difference agreed very well with gravimetric maleic anhydride results. Short-cut infrared procedures for the rapid determination of key components were described by Seyfried (205). The principles of mass spectrometry and its applications in hydrocarbon gas analysis were described by Washburn (235) and its application to plant hydrocarbon problems, by Roberts (192). Commenting on results obtained by cooperating laboratories which applied mass spectrometry to the analysis of a standard sample of natural gas, Shepherd (209) concluded that the reproducibility is better than with chemical methods. Johnsen (108) avoided the need for the customary pressure measurement in mass spectrometric analysis by employing the ratio of the peaks of the two components, in binary mixtures. Electrical computing instruments to solve the simultaneous equations associated with mass spectrometry and absorption spectrometry were described by Morgan (167). Turkevitch (224) reported on a study to determine the position of the tracer atom in deuterated hydrocarbons.

D'Ouville (59) employed thermoconductivity cells for gas analysis in studying synthesis of hydrocarbons. Starr (215) in a study of low temperature fractional distillation showed that much faster charging rates and distillation rates than are customary can be employed, without loss in precision.

GASOLINE

Because gasoline is such a complex and important mixture of hydrocarbons, distillation is frequently used to produce fractions of much lesser complexity for further examination by other means, and this has resulted in the development of numerous high-efficiency fractionating apparatus and methods.

Selker (204) described a low holdup concentric glass tube column of high efficiency, capable of handling small samples. Baker (12) studied a number of popular fractionating columns and concluded that the spinning band type is particularly good for small samples. Lecky (125) showed excellent results with a column packing consisting of a long continuous nickel gauze spiral wound around a glass tube. Bragg (30) compared concentric glass tube columns, glass bubble cap columns, empty glass columns, and Stedman columns packed with several forms of wire cloth packing. Schaffner (198) described a rectifying unit claimed superior for low pressure distillations, involving alternately heated and cooled zones in the distilling tube. Todd

(222) reported the characteristics of an adiabatic distillation unit the column of which is packed with metal spiral packing, and claimed it suitable up to 400° C. at atmospheric pressure or in vacuum. Langdon (124) claimed numerous advantages for a rather unconventional column in which the feed is charged at the top and the higher boiling fraction is removed at the bottom. In a symposium on high temperature analytical distillation, experiences with apparatus and methods were reviewed by Reed (186, 187), Goldsbarry (81), Donnell (58), Borns (26), Marschner (159), Hall (89), Brandt (31), Willingham (242), and Collins (44).

Automatic analytical distillation units were described by Steffens (216), Smith (211), and Melpolder (162). The separating possibilities of azeotropic distillation were excellently reviewed by Mair (155) and Ewell (65), and vacuum and molecular distillation by Hickman (94), and a general review was presented by Walsh (233).

Thermometric methods were used by Corson (47) and Bishop (22) to determine aromatic hydrocarbons in cycloparaffins; by Sefton (203) to determine cyclopentadiene in aromatic hydrocarbons; and by Cerveny (41) to determine naphthalene, Tetralin, and Decalin in a ternary mixture. Benzene was detected and determined in other aromatic hydrocarbons by Dolin (56) on the basis of the intensity of the red reaction product obtained when the sample is nitrated, and extracted with ether and the extract is treated with butanone and alcoholic sodium hydroxide followed by acetic acid; the acetic acid eliminates the interfering colors produced by the homologs. Gambrill (75) determined the aromatic content of aviation gasoline from the solubility of picric acid in the mixture, applying corrections for olefins and naphthenes.

The outstanding possibilities of chromatography in hydrocarbon analysis were demonstrated by Mair (152), who determined aromatic hydrocarbons in gasoline by percolation through a column of silica gel, following the change in nature of the percolate by refractive index on small successive fractions leaving the bottom of the column; by a modification determined aromatics and mono-olefin hydrocarbons (151); and extended the technique to higher boiling hydrocarbons such as kerosene (153), for which he employed a 52-foot adsorption column. The adsorption technique has been used by Dinneen (55) for the examination of naphtha derived from shale oil and Conrad (45) has modified the method of Mair to render it faster and simpler by a technique involving ultraviolet radiation and measurement of zones in the column, to avoid the necessity of refractive index determinations. Kurtz (121) analyzed gasoline for hydrocarbon types by testing distillation fractions for bromine number and solubility in a mixture of phosphorus pentoxide and strong sulfuric acid, and provided methods for cross checking the data. Mills (166) reported refinements in this procedure for determining total aromatics plus olefins. Berg (19) used a mixture of sulfuric and acetic acids to determine aromatics plus olefins, and claimed this reagent extracts the olefins completely. To avoid the complications of olefins when gasoline fractions are analyzed for aromatic hydrocarbons, Love (141) brominated the sample and removed unreacted hydrocarbons by steam distillation. The distillate was treated with strong sulfuric acid to constant refractive index; the change in refractive index was a measure of the aromatics and the refractive index at constant value the basis for computing paraffins and naphthenes.

The capacity for adding halogen has been extensively used as a measure of unsaturation in hydrocarbon analysis. Lewis (131) employed a modification of the bromide-bromate method to determine bromine addition number, claiming speed and simplicity; sulfur compounds interfere, resulting in low bromine numbers. Uhrig (226) dissolved the sample in chloroform and titrated directly with bromine in glacial acetic acid to the orange-yellow end point of an excess of bromine and reported that the solvents employed are factors in the determination. Jordan

(*112*), studying the method of Kaufman (bromine in methanol and sodium bromide) and the method of McIlhiney (bromine in carbon tetrachloride) on styrene and indene found, anomalously, that half the consumed bromine appeared as hydrobromic acid in the Kaufman method but obtained very little hydrobromic in the McIlhiney procedure. Another modification of the bromide-bromate method for determining unsaturation was described by Johnson (*109*), who found it suitable for petroleum products boiling below anthracene (this method has been adopted by A.S.T.M. for the analysis of petroleum products). An electrometric version of the bromide-bromate method was described by DuBois (*60*) who worked at ice temperature and employed a dead-stop end point. The method was shown to be more reliable than visual titration, particularly on samples containing high boiling aromatic hydrocarbons.

Joshel (*114*), finding the usual halogenation methods and methods involving potassium permanganate or perbenzoic acid unsuitable for unsaturation of hydrocarbons in the terpene series, adopted a hydrogenation procedure involving acetic acid as solvent and palladium as catalyst. From studies of unsaturation in isoprene-isobutylene copolymers, Gallo (*74*) claimed a superior method involving iodine–mercuric acetate in trichloroacetic acid as reagent. This solvent apparently accelerated the halogenation.

Bond (*25*) employed nitrogen tetroxide for a less indirect determination of unsaturated hydrocarbons in the gasoline range. The reagent forms products of low volatility from which the unreacted hydrocarbons are recovered by steam distillation and measured. Bond (*24*) also made a direct determination of styrene in complex mixtures in the naphtha range by reaction with nitrous acid, weighing the crystalline styrene nitrosite; most other unsaturated hydrocarbons do not interfere. Cyclopentadienes in mixtures with other hydrocarbons were depolymerized by Powell (*179*), who determined the composition of the monomers promptly on the basis of the difference in reaction rate with acetone and with benzaldehyde to produce colored fulvenes whose intensities were measured with a spectrophotometer. Both cyclopentadiene and methylcyclopentadiene react promptly with benzaldehyde but the reaction rates are very different with acetone. Bergmann (*20*) determined dicyclopentadiene from the saponification value of the esters that result when it is refluxed with an excess of formic acid.

Lipkin determined the nature of hydrocarbon mixtures from relatively easily determinable physical properties; naphthene rings in mixtures of paraffins and naphthenes (*137*) from a correlation of density or refractive index and the temperature coefficient of density, and claimed applicability to samples of wide boiling range. He derived equations for calculating refractive index and density (*136*) with rather good accuracy. Density and temperature coefficient of density formed the basis of his method for determining the proportion of ring and chain for aromatic molecules (*135*) and when applied to pure compound data rather good results were obtained. He proposed an equation for double bond index (*138*), claimed useful for classifying and identifying aromatic or olefinic types in petroleum fractions without interference by paraffins and naphthenes. It involves specific dispersion, molecular weight, and number of double bonds per molecule; simple means for obtaining these data indirectly are given.

Instrumental methods of analysis have found very extensive application in the field of gasoline analysis. Groennings (*85*) modified the specific dispersion method of Grosse and Wackher for determining aromatic hydrocarbons in gasoline, by providing more specific corrections for the interference of different classes of olefins. Hindin (*97*) employed an Abbe type instrument and white light to obtain refractive index which in conjunction with density enabled him to determine whether a saturated sample was substantially aromatic. Polarographic methods were used by Laitinen (*122*) for determining olefins and acetylenes and by Burdett (*38*) for naphthalenes in petroleum fractions. Jones

(*111*) discussed the utility of ultraviolet spectra and the effect of structure and gave references to absorption spectra of hydrocarbons. Schnurmann (*201*) discussed the application of ultraviolet absorption to analysis of mixtures of close boiling aromatics, emphasized the need for standardization, and stressed the importance of rigorously treated solvents for this type of investigation. Cole (*43*) claimed that for samples of low benzene concentration, ultraviolet absorption of the vapors serves better to measure benzene in toluene than the liquid. This author used an interferometer to determine toluene in air.

Barnes (*15*) and Brattain (*32*) discussed the principles and the mechanism which make infrared absorption analysis possible. (The latter, *33*, described an infrared spectrophotometric method for the quantitative analysis of gaseous mixtures of C_4 hydrocarbons.) The qualitative compositon of the sample must be known and not more than about nine constituents may be present at one time. Nitroparaffins were analyzed by infrared absorption by Nielsen (*173*), who used a variable-thickness cell. Kent (*115*), Heigl (*92*), and Webb (*237*) described methods for analysis of hydrocarbon mixtures in the gasoline range, involving distillation into fractions, each of which contains a relatively small number of constituents, followed by infrared absorption analysis of the fractions. Herald (*93*) determined the composition of a blend of iso-octane and *n*-heptane, used in knock testing, by infrared absorption analysis and Anderson (*8*) described an infrared procedure for determining impurities in commercial iso-octane used in knock testing; the impurities totaled as many as 8 in number and their sum was 0.5% maximum. Johnston (*110*) working on refinery products in the gasoline range used silica gel to adsorb, concentrate, and separate the olefins from other hydrocarbon types and applied infrared absorption analysis to a fraction of the material desorbed from the gel, differentiating α-olefins from olefins with internal double bonds. Avery (*11*), studying the infrared spectra of trimethylpentanes at temperatures of 0° and −195° C., pointed out the advantages of the lower temperature at which narrower band widths are obtained.

Grosse (*86*) identified certain narrow distillation fractions as paraffins by comparing their Raman spectra with those of pure hydrocarbons and observed that the intensity of the Raman lines is proportional to the concentration of the hydrocarbons, visual estimation being useful in binary and ternary mixtures. Interfering substances were eliminated by treatment with reagents or hydrogenation. Rank (*182*) emphasized the possibilities of analysis by Raman spectra and obtained the spectra of numerous hydrocarbons. Fenske (*66*) gave the spectra of a large number of hydrocarbons, suitable for qualitative and quantitative analytical utilization. Glockler (*79*) reviewed a number of papers on the theory of the Raman effect and related topics. Rosenbaum (*195*) discussed the application of Raman spectra to the quantitative analysis of hydrocarbon mixtures and described a semiempirical procedure to simplify the method.

Brown (*36*) applied the mass spectrometer to the analysis of normally liquid hydrocarbons (C_5 to C_8) but was handicapped by the unavailability of the pure hydrocarbons necessary for calibration. Taylor (*219*) reported experiences in extending the use of the mass spectrometer to mixtures of organic compounds in both liquid and gaseous condition, including oxygenated compounds, aromatics, halides, sulfur compounds, and C_6 to C_9 hydrocarbons. Roberts (*193*) presented the mass spectra of numerous organic compounds as an aid in analyzing mixtures of them. Bloom (*23*) compared the mass spectra of numerous isomers of octane, studied the effects of groupings, and concluded that the deduction of structure of complicated molecules by mass spectrometry is far from realization.

The joint effort of the American Petroleum Institute (Research Project 44) and the National Bureau of Standards (*170*) resulted in a wealth of information useful in analysis. This comprised the compilation of fundamental data on physical and thermodynamic properties of hydrocarbons and infrared, ultra-

violet, Raman, and mass spectrograms of many pure hydrocarbons.

Wagner and co-workers (230-232), studied a number of popular methods for determining peroxides in hydrocarbons, including those involving iodometric reagents, ferrothiocyanate, and ferrous-titanous reagents.

A colorimetric method for determining aminophenol and phenylenediamine inhibitors in gasoline, involving phosphotungstic acid, was described by Williams (241).

The important problem of determining tetraethyllead in gasoline continues to intrigue investigators. Schwartz (202) modified the Baldeschwieler procedure to employ a mixture of nitric acid and potassium chlorate for bringing the lead into aqueous solution. The determination was completed gravimetrically or by titration; speed and accuracy are claimed. Gonick (82) treated gasoline with a solution of iodine in carbon tetrachloride to convert the lead to inorganic form and after several operations completed the determination alkalimetrically. Lykken (144) made an exhaustive investigation of existing methods for determining lead in gasoline and proposed two new methods which involve direct evaporation of sample with hydrochloric acid or iodine reagent. The determination is completed iodometrically after addition of an excess of dichromate solution. Gordon (84) also employed iodine in a microdetermination. Newman (172) described a rapid method of rather limited application, involving an excess of alcoholic potassium triiodide; the excess of iodine was determined with thiosulfate. The method is claimed applicable primarily to ordinary aviation fuels, for highly unsaturated stocks interfere. Borup (27) described a polarographic method for which simplicity of operation is claimed.

KEROSENE AND HEAVIER FUELS

Because of the greater complexity of the hydrocarbon mixtures in the fuels boiling above gasoline, aniline point dissolution temperature is commonly used as a coarse indication of paraffinicity. Matteson (161) employed infrared radiation and a sensitive photocell to recognize the dissolution temperature of dark petroleum products and aniline. Williams (240) determined the aniline point of dark oils with a special glass cell where the layer of liquid was approximately 2 mm. thick. The observation was made with the unaided eye. Brown (35) determined the aniline point of petroleum products with a semiautomatic device involving the use of an electric eye; the method was equally useful for light colored oils.

Rescorla (189) studied numerous tests reported for determining the stability of fuel oils. The methods include simple evaporation at high temperature, controlled oxidation, determination of insolubles, or acid treatment to determine reactive substances. The author concludes that a special resin test and acid flocculation are best.

LUBRICATING OIL

Deanesly (53) described a method for determining the hydrocarbon type composition of oils and claims it is more accurate and more widely applicable than the Waterman method. It is based on determinations of aromaticity or unsaturation of the sample, the structure of the sample when completely saturated, density, refractive index, specific dispersion, bromine number, molecular weight, and carbon and hydrogen ratio. Lipkin (134) modified the silica gel adsorption method of Mair to render it suitable for the determination of aromatics in higher boiling fractions. A solution of the sample in pentane is percolated through the gel and the aromatics are desorbed with a mixture of benzene and methyl alcohol; evaporation of the solvents leaves the aromatics as residue for weighing. The method was used for gas oil and lubricating oil.

A manometric method for determining water in insulating oil, based on change in vapor pressure of lithium chloride before and

after exposure, was used by Evans (64). Aepli (2) described an apparatus in which the sample can be taken from a stream and its water content determined by titration with Fischer reagent without exposure to the atmosphere. Acker (1), using Karl Fischer reagent to determine water in oil, employed direct titration electrometrically and claimed that back-titration procedures with Fischer reagent introduce an uncertainty because of the instability of the reagent. Radioactive hydrogen (tritium) was employed by Joris (113) in determining the solubility of water in hydrocarbons, by measuring radioactivity of the solution.

Methods for studying oxidation stability of lubricating oils under catalyzed and stirring conditions were described by Lamb (123) and Loane (140) and comparisons were made with engine experiences on the same oils and between stability and concentration of inhibitor. A corrosion test employing a ratio of oil volume to bearing surface, similar to that found in full scale engines and operating under dynamic conditions, is described by MacCoull (146), who reports correlation with multicylinder engine behavior. A catalyzed oxidation-corrosion test which is claimed to give good correlation with performance, is described by Pope (177).

A method for determining oil in wax with methyl ethyl ketone as solvent is described by Lee (126). Benjamin (18) employed a fluorescence method for determining oil in blends with other oils and in oil-water emulsions.

A very exhaustive examination of used engine lubricating oils and a review of the methods employed to analyze them are given by Hilfreich (95).

ASPHALT

Asphalt was recovered from road materials by Ford (69) by extraction with benzene or carbon disulfide and distillation of the solution in an atmosphere of carbon dioxide at atmospheric pressure. The method is compared with the Abson and Siegmann methods. Knowles (117) determined wax in asphalt by eliminating the asphaltene-resin fraction with liquid propane at elevated temperature and determined the wax on the propane soluble matter with methyl isobutyl ketone at low temperature. This method avoids the losses of wax, due to destructive distillation, of the Holde method. Methods for determining the components of asphalts-asphaltenes, resins, oils, etc., are described by Strieter (217), Hoiberg (101), and Hubbard (105). Cropper (49) determined small amounts of anthracene in tars, etc., by chromatography with alumina as adsorbent, isolating the band containing anthracene, recognized by fluorescence in ultraviolet, and its subsequent solution in chlorobenzene. The optical density of this solution at 380 and at 370 millimicrons was the basis of the determination.

Anderson (7) described a rather novel viscometer with which viscosities can be determined on a wide range of asphaltic products at one temperature. Its principal feature is the use of three capillaries of decreasing bore arranged in series with intervening bulbs, the widest capillary at the bottom for most viscous samples and the narrowest at the top for the least viscous. The viscometer is cleaned without removal from the bath by drawing solvent through it. Young (243) found the Gardner-Holdt air bubble viscometer satisfactory for determining viscosities of high polymers in volatile solvents.

SPECIALTIES

Webber (238) reviewed methods for quantitative analysis of grease and Barnett (16) suggested numerous improvements in the A.S.T.M. method. A number of rapid methods for grease analysis claimed suitable for plant control were described in a report of an A.S.T.M. committee (5). A disk viscometer for determining the apparent viscosity of a few milligrams of liquid or plastic samples was described by McKibben (148). The sample is placed on one of two disks, one of which turns against

the other under spring tension, and the torque transmitted to the stationary disk is measured.

A rapid method for the volumetric determination of organic sulfonates in detergents was described by Marron (158). The reagent is p-toluidine hydrochloride and ends by alkali titration of the organic sulfonate. Brooks (34) analyzed oil-soluble petroleum sulfonates by adsorption on Attapulgus clay. A method for the analysis for oil-soluble petroleum sulfonates, involving countercurrent extraction, etc., was recently adopted by A.S.T.M. (6).

Burchfield (37) and Parker (175) described methods for identifying natural and synthetic rubber and rubberlike polymers by simple laboratory techniques. The former involves pH and gravity of pyrolysis products and the latter involves time of reaction in an acid decomposition of the sample.

POLLUTION

Gilber (77) determined aromatics in air by extracting a large sample with methyl alcohol to dissolve the aromatics, which were then determined from the refractive index of the solution. Coulson-Smith (48) determined acetylene in air colorimetrically using ammoniacal cuprous chloride as reagent following removal of hydrogen sulfide and phosphide by passage of the air through a tube containing paper impregnated with copper sulfate. Geissman (76) modified the method of Coulson-Smith, employing a photoelectric colorimeter for measuring color intensity, and used standards made of air-acetylene mixtures. Mikita (163) studied gasoline engine exhaust odors and described a colorimetric method for aldehydes involving Schiff's reagent which correlates with nasal evaluations of the pungent odor of exhaust gases. Noll (174) modified the method of Scott for determining oil in water by "fixing" the sample so the oil does not separate on standing, by ammoniacal precipitation of iron hydroxide from specially prepared ferric chloride and extracted the oil, occluded in the hydroxide, with ether. Small amounts of aromatic hydrocarbons in aqueous solutions were determined by Morris (168) by extraction with carbon tetrachloride followed by treatment with formaldehyde–sulfuric acid reagent; the brown coloration was a measure of the aromatics. Lykken (145), working on hydrocarbon mixtures, determined phenols by dissolving them in acetic acid and making nitrosophenol, which upon rendering ammoniacal gave a colored quinoid, the intensity of which was measured with a photoelectric colorimeter. It is important to select for standardization a phenol corresponding to that present in the unknown. Lisle (139) described a simple test involving silver nitrate–methylene blue test paper upon which many carcinogenic hydrocarbons are stated to produce a blue color upon irradiation at 4300 Å. units.

ELEMENTS

The use of additives, inhibitors, and newer production processes has added importance to the determination of elements characteristic of these additives, etc., and the study of used oils has also contributed. Agruss (3) determined halogens in mineral oil by combustion in a Parr oxygen bomb containing sodium bicarbonate solution in which the halogen is determined by titration with silver nitrate. He also used digestion with alcoholic potassium hydroxide to recognize types of halogen combinations and digestion with alcoholic solutions of thiourea to yield derivatives which are subsequently converted to picrates for identification. Elving (63) fused the sample with an alkali metal in an evacuated steel tube and determined the halide by conventional methods. Huckabay (106) described a special combustion procedure for determining traces of fluorine in organic compounds; the fluorine reaction product was absorbed in aqueous reagent where it was determined with sodium alizarin sulfonate indicator. Levin (128) determined phosphorus by ignition with sodium naphthenate, conversion of the ash to orthophosphate, and precipitation

as phosphomolybdate, the volume of precipitate on centrifuging being a measure of phosphorus content.

Hindin (99) adapted the lamp sulfur method to the precise determination of hydrogen in liquid organic compounds, collecting and weighing the water, and used the hydrogen values (98) for calculating the naphthene-paraffin composition of a mixture of these hydrocarbon types resulting from analysis of gasoline. The lamp combustion procedure was extended by Simmons (210) to the determination of carbon and hydrogen in petroleum distillates with excellent precision. The products of combustion—water and carbon doxide—were absorbed in the customary manner. Clark (42), studying carbon and hydrogen microdetermination, emphasized the importance of preburning to ensure purity of the oxygen and the need for high catalyst activity to ensure complete combustion of oxidation-resistant mineral oils. Small amounts of oxygen in organic compounds were determined by Walton (234) by a modification of the Unterzaucher procedure whereby pyrolysis is conducted in an atmosphere of helium over carbon pellets at 1120° C. and the carbon monoxide is collected and determined colorimetrically by means of an indicating gel. As little as 0.01% of oxygen is determinable.

Assaf (9) determined copper in oils after wet oxidation, by titration with dithizone. Rittershausen (191) extracted the metallic elements from oil and grease by refluxing with hydrochloric acid in a special extractor and analyzed the extract by conventional methods, claiming that the extraction procedure yields more reliable results than those based on ignition. Emission spectrometry was used by Calkins (40) to determine metallic elements of additives in lubricating oils; graphite electrodes were saturated, under special conditions, with the oil under test and then sparked in the usual manner. Emission spectrometry was used by Burdett (39) and Marling (157) for the determination of contaminants and minor constituents of silica-alumina cracking catalysts. Russell (196) reviewed the applications of emission spectrometry to samples in a petroleum laboratory.

SULFUR AND ITS COMPOUNDS

Ball (14) described a system of analysis for determining types of sulfur compounds in petroleum distillates, claiming the method to be an improvement but admitting its inadequacies. Koons (120) determined mercaptan (thiol) sulfur in refinery caustic scrubbing solutions by acidification, extraction with naphtha, treatment with an excess of standard silver nitrate, and determination of the excess by titration with ammonium thiosulfate to ferric ammonium sulfate indicator. Tamele (218) determined mercaptans in aqueous alkaline solutions potentiometrically with silver nitrate, using a polished silver rod or one coated with silver sulfide as indicator electrode; interferences are discussed. Schindler (200) found that preliminary removal of free sulfur by conversion to mercuric sulfide, before titrating mercaptan sulfur in naphthas with silver nitrate, is conducive to low results, apparently because mercuric sulfide adsorbs mercaptan. Pompeo (176) described a semiautomatic electrometer and method for determining mercaptan sulfur in plant control of gasoline sweetening operations, Davies (51) described a potentiometric method for mercaptan sulfur without interference by elementary sulfur, and Kolthoff (118) titrated mercaptans with silver nitrate amperometrically, employing a rotating platinum electrode.

To detect hydrogen sulfide, Behrens (17) passed the gas over a lead acetate tape which moves between a light and a photocell on which it is focused, reduction in transmission due to lead sulfide causing an alarm to sound. Shaw (207), employing a special flask, determined hydrogen sulfide and mercaptan by passing the gas through cadmium chloride for both and through acidified cadmium chloride for hydrogen sulfide. Field (68) determined hydrogen sulfide colorimetrically with uranyl cadmium reagent, analysis being made by visual comparisons; and also spectrophotometrically after production of a bismuth sulfide suspension.

French (73) and McKee (147) made improvements in the isatin test for thiophene and Hartough (91), studying the application of a ceric nitrate test, concluded that it can be used to distinguish some thiophenes but in general can not be relied upon to distinguish individual thiophene derivatives.

Kolthoff (119) employed amalgamated zinc in a Jones reductor to reduce disulfides to mercaptans which were subsequently determined amperometrically by titration with silver nitrate; mercaptans initially present were removed first by precipitation with silver nitrate. Carbon disulfide in benzene was determined colorimetrically by Dick (54) with diethylamine and copper acetate as reagents. Levin (130) determined free sulfur in lubricating oil by reaction with copper gauze from which the hydrogen sulfide is subsequently liberated, collected in cadmium chloride, and determined iodometrically. Brady (28) determined thiophene, carbon oxysulfide, and carbon disulfide in producer gas spectrophotometrically by measuring ultraviolet absorption after treatment with selective reagents.

Total sulfur in organic compounds was determined by Theilacker (220) by a modification of the hydrogenation method of ter Meulen, on a semimicro scale; the hydrogen sulfide was absorbed in zinc acetate, and the determination completed iodometrically. Luke (143) determined total sulfur in rubber by wet oxidation to sulfate, reduction to sulfide, liberation of hydrogen sulfide, and its determination iodometrically. It is claimed that unlike gravimetric methods this procedure is applicable to samples containing barium, lead, etc. Hinckley (96) determined total sulfur in naphthalene by combustion in purified air and turbidimetric determination of barium sulfate. Hagerman (88) determined total sulfur in organic materials by passing them downward through a heated vertical stainless steel tube packed with quartz and sand, collecting the resulting sulfur gases in hydrogen peroxide, and completing the determination alkalimetrically; simplicity of operation is claimed. Thiosulfate in used doctor solution was determined by Uhrig (227) by precipitation of the lead with carbon dioxide, addition of formaldehyde to eliminate interference of sulfite, and titration with iodine after acidification with acetic acid.

CATALYSTS

Webb (236) discussed precautions to be taken in determining particle size distribution of silica-alumina catalysts by mechanical screening and liquid sedimentation methods. Various methods of evaluating cracking catalysts were reported at a symposium of the American Petroleum Institute by Innes (107), Matheson (160), Wiley (239), Mills (165), Scheumann (199), Pratt (180), Ray (184), Alexander (4), Shankland (206), McReynolds (150), Rice (190), Berkhimer (21), Hornaday (102), and Grote (87). Numerous methods for evaluating cracking catalysts were also reviewed by Rescorla (188). Goff (80) described a procedure with Fischer reagent for determination of water in the sulfuric acid alkylation catalyst.

MISCELLANEOUS

Mair (154) and Glasgow (78) described a method for determining freezing point and its use in estimating impurities, attaining a high degree of precision and reliability. Freezing point has been used to determine impurities in styrene by Smoker (212) and by Ray (185) to determine the purity of low purity dicyclopentadiene after adding to it high purity dicyclopentadiene to raise the over-all concentration of the mixture enough to make a freezing point technique applicable. Aston (10) described a melting point calorimeter for evaluating purity of organic material. Maclean (149) claimed that ultraviolet spectrophotometry is sometimes more sensitive than other physical means for determining uniformity of solvents and used ultraviolet absorption curves to detect impurities.

Lipkin (133) described a pressure viscometer for propane and butanes. Zeitfuchs (245) described a viscometer suitable for

opaque and very viscous liquids. Hoiberg (100), measuring the time required for a drop of sample to fall a fixed distance in a mixture of alcohol and water of suitable proportions, attained a high degree of precision for density determination. The method was applicable to very small samples. Forziati (70) described the assembly and calibration of a density balance for very high precision on small liquid hydrocarbon samples. Kirby (116) employed Barger's isotonic method for determining the mean molecular weight of bitumens, resins, oil, etc. Young (244) determined molecular weight of gasoline hydrocarbons by vapor density with a vacuum micromanometer which he describes. The determination is made at room temperature and an absolute pressure of less than 1 mm. of mercury. Improvements in the determination of thermal value of gasoline in an oxygen bomb calorimeter are described by Levin (129), Dean (52), and LeTourneau (127); each involves very simple modifications of conventional methods.

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Pharmaceuticals and Natural Drugs

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THE war years and those immediately following have witnessed much progress in analytical chemistry as it is applied to pharmaceutical and natural drug fields. The coming of age, as it were, of instrumentation and the application of physicochemical methods of isolation and measurement have provided the analyst with new approaches and new techniques. These new methods enable him to measure the potency of crude and raw drugs in their natural state and to determine more precisely the concentration of the active ingredients in finished pharmaceutical preparations.

The thirteenth revision of the United States Pharmacopoeia and the eighth revision of the National Formulary, the official compendia which co er the manufacture, compounding, and dispensing of medicinal preparations, became official April 1, 1947. Both contain many new and many improved analytical procedures for the large number of items listed. The U. S. Pharmacopoeia XIII (*199*) has for the first time given official recognition to ultraviolet absorption methods, and colorimetric controls for digitoxin and has recognized refractive indexes of some of the U.S.P. crystalline substances, as reported by Keenan (*116*).

In that section of the National Formulary (*151*) describing general tests, processes, and apparatus are new procedures for determining alkali salts of organic acids, chloroform, light transmission, fineness of powders, nitrate assay by nitrometer method and nitrogen by both the Kjeldahl and the semimicro-Kjeldahl methods, and the listing of color names as determined by the I.S.C.C.–N.B.S. method.

In the field of antibiotic drugs and some vitamins, biological and microbiological methods of estimating the potency play a predominant role. In general, most of the standard reference samples that are available for evaluating unknown preparations have been standardized by these methods; thus the accuracy of many of the chemical or physicochemical or physical methods may be limited by the accuracy of the biological or microbiological methods that are used to standardize the respective reference samples.

As a basis for further discussion of the various analytical procedures used in the pharmaceutical field three broad classifications might be utilized: (1) methods that depend upon strictly chemical reactions and chemical equivalents for measuring a specific substance—i.e., determinations of a halogen by titration with standard silver nitrate solution; (2) methods that involve both chemical reactions and physical means of measuring the resultant product or products—i.e., formation of a color due to a chemical reaction and a measurement of this color by suitable photoelectric instruments; and (3) the various physical methods of analysis, such as microscopic, polarimetric, ultraviolet absorption, and solubility.

CHEMICAL METHODS

ALKALOIDS AND RELATED SUBSTANCES

A modified semimicro Zeisel apparatus has been used by Green and Green (*89*) to determine acetophenetidin from the ethoxy content in mixtures of aspirin, acetophenetidin, and caffeine. The ethyl iodide formed is collected in a bromine–potassium acetate–acetic acid mixture whereby iodate is formed and ultimately determined with thiosulfate. The aspirin is determined by extraction with sodium bicarbonate and subsequent bromination with Koppeschar's reagent. After the total chloroformic extractive containing acetophenetidin and caffeine has been weighed, the caffeine is determined by difference.

The U. S. Pharmacopoeia recognizes a method for determining the total crystallizable cinchona alkaloids of totaquine and

procedures for the elimination of stearic acid and stearates in the assays of barbital and phenobarbital tablets and in many of the other tablets listed therein. In another approach to the removal of interfering substances Anderson (*4*) has proposed the use of enzymatic digestion of colchicum corm to facilitate its assay. The quantitative recovery of colchicine is comparable to the procedure now official.

Levine (*129*) uses a microchemical identification test for demerol, which involves a formation of crystals with alkaloidal reagents. He also describes the reaction of demerol with picric acid, lead iodide, sodium nitroprusside, potassium iodide, and potassium dichromate. Further identification techniques are described by Haley (*93*), who proposes methods for the identification and differentiation of isomers of desoxyephedrine from each other and from twelve sympathomimetic amines. He recommends chloroauric, chloroplatinic, and picric acids, which give crystalline precipitates with definite melting points.

The distillation of ephedrine alkaloid from strong caustic solutions rather than extraction with an immiscible solvent is suggested by Schoen (*172*) and Hilty (*100*), and Welsh (*204*) has described a method by which ephedrine may be separated from procaine by forming the *N*-acetyl derivative. The acetyl derivative may be extracted with chloroform from an acid medium and weighed and the procaine may then be determined by making the aqueous solution ammoniacal and subsequently extracting with chloroform.

Several modifications of the official methods for the assay of ipecac and of ipecac preparations are described by Whipple and Woodside (*206*). The assay results of each modification on a given sample are recorded and a general method of assay applicable to ipecac and its preparations and with fewer inherent sources of error than those of any official method is recommended.

The reaction of theophylline with various barbiturates has been studied by Higgins and Dunker (*98*), who suggest identification tests for either phenobarbital or theophylline which involve reaction of the two in alcohol to form a compound containing 2 moles of theophylline and 1 mole of phenobarbital. This particular compound is reported to have a specific melting point (250.7° to 251.7° C.) and the reaction appears to be specific for both compounds. Nineteen other barbituric acid derivatives were treated in the same manner and none gave the same product.

In the natural drug field Basu and Pabrai (*17*) have isolated and described two new alkaloids, celastrine and paniculatine from *Celastrus paniculta Willd.* Spaeranthine, another alkaloid, along with a volatile oil has been isolated from *Spaeranthus indicus* by Basu and Lamsal (*16*), who also describe the physical and chemical properties of these newly isolated principles. Further work in the natural drug field includes a study by Oneto (*154*) of six species of Garrya. He reports that all contained alkaloids and that two crystalline substances were obtained from the bark of one species. A number of salts from these crystalline substances have been prepared and analytical data are given for these two crystalline substances.

ANTIBIOTICS

Analysis in the field of antibiotic manufacturing and development changes so frequently and is developing so rapidly that it is almost impossible to be well informed on the latest procedures. All antibiotics are under the control of the Federal Government and the final product of each lot of finished material must be certified by the Federal Food and Drug Administration before it can be marketed. The regulations for tests and methods of analysis of antibiotic (penicillin and streptomycin) drugs are

outlined in the *Federal Register* (*67*). These procedures, however, do not cover the intermediate phases of the actual production.

Microbiological methods are apparently the only foolproof methods of assay for the actual potency determination of all the antibiotics and are used almost exclusively in the early development of any antibiotic. These methods utilize the inhibiting effect of the biologically active substance on certain microorganisms, thus paralleling their use in the treatment of certain infections. Chemical means of determining the potency of an antibiotic are made more difficult, because many of the antibiotics occur as mixtures of several types of the same antibiotic. Penicillin, even in the crystalline state, may be composed of several chemically closely related substances—namely, penicillin F, dihydro F, G, X, and K. Likewise, the streptomycin complex consists of streptomycin (*N*-methyl-1-glycosaminido-streptosidostreptidine), mannosidostreptomycin (formerly called streptomycin B), and probably other streptomycinlike substances.

The iodometric method for the estimation of penicillin as used by the Federal Food and Drug Administration and described by Alicino (*2*) is satisfactory but at times erroneous results are obtained. Wild (*209*) has studied the weaknesses of this method and has summarized the errors encountered. Mader and Buck (*134*) have proposed a chemical method for the determination of penicillin G. In this procedure the penicillin G is precipitated with *N*-ethylpiperidine and the precipitate is dried and weighed. This is the method used by the Federal Food and Drug Administration for the determination of penicillin G on samples submitted for certification but it is not valid for samples containing more than a very small percentage of penicillin X.

CHEMOTHERAPEUTIC AGENTS

A bromination method for the determination of sulfonamides in which the excess bromine is determined with arsenic trioxide is suggested by Conway (*47*). The advantages of this method as listed by the author are: All operations are at room temperature; acetylated sulfonamides need not be hydrolyzed; no external indicator is needed; and the end point is sharp and stable. Tables to compare with U.S.P. assays are also given.

METALLIC IONS AND RELATED SUBSTANCES

The U. S. Pharmacopoeia XIII recommends the use of nitrobenzene in the chloride determination with silver nitrate rather than filtering off the silver chloride precipitate. It also has changed the methods for determining iodine in sodium iodophthalein and calcium iodobenhenate to the silver iodide volumetric method. The method for iodine in thyroid preparations has been materially improved by the use of a solid potassium carbonate fusion. Iodine in iodized oil is now determined by sodium carbonate fusion and subsequent determination with silver nitrate rather than potassium iodate.

Bandelin (*9*) has proposed a method for the determination of aluminum in pharmaceutical preparations which is dependent upon the gradual evolution of ammonia from urea in boiling acid solution containing succinic acid. Aluminum is precipitated quantitatively as the basic succinate, filtered, and ignited to alumina.

An assay method for the determination of arsenic described by Waters *et al.* (*202*) is applicable to six of the seven U.S.P. arsenicals. The method employs an alkali-acid permanganate oxidation for the destruction of organic matter. Techniques of wet combustion of organic compounds and methods for estimating arsenic were studied by Banks *et al.* (*13*) in an effort to formulate a single procedure which would combine the features of universal applicability, ease of operation, and a high degree of accuracy.

Six variations of procedure were evolved and compared with two standard procedures against analytically pure *p*-arsenic acids. Three of the six variations were selected for further examination. No one method would suffice for all arsenic compounds. One variant, however, was satisfactory for those arsenicals used as drugs. Representative official preparations were assayed by this method and the results indicate that the new procedure is applicable for all official arsenicals.

Jorgensen (*111*) has compared several methods for the determination of arsenic and pentavalent arsenicals alone and in combination with bismuth. He concludes that the official A.O.A.C. method is more accurate and yields more consistent results under all conditions than any other procedure.

A method involving the use of 8-hydroxyquinoline for the separation of bismuth at a pH of 5.2 to 5.4 in the presence of magnesium, which is determined in the filtrate is reported by Haynes (*96*). In another method of analysis Osborn (*155*) has separated calcium from barium and strontium by preparing the sulfates of these three constituents and filtering off the insoluble barium and strontium sulfates.

Methods for the determination of iodine in organic compounds have been reviewed by Block and Waters (*26*), who conclude that the method of Johnson and Frederick is applicable to most pure organic compounds. They also propose a procedure using a mixture of sodium carbonate, potassium carbonate, and manganese dioxide as an ignition mixture and then leach out the soluble iodide with water. The iodide is oxidized with bromine to iodate and after the addition of potassium iodide the liberated iodine is titrated with sodium thiosulfate. This procedure appears to be general for all but the most volatile organic iodine compounds. In further studies of iodine compounds Waters and Beal (*201*) describe, in a series of three articles, the stability of the iodine content of desiccated thyroid and the determination of water-soluble inorganic iodide in thyroid and propose a modification to the U. S. Pharmacopoeia XII method for the determination of iodine in thyroid by using potassium carbonate as the ignition mixture and determining the iodide as described by Block and Waters (*26*).

The determination of magnesia in magnesium sulfate and solution of magnesium citrate has been reviewed by Goldstein (*84*). He compares the oxine and pyrophosphate procedures and recommends precipitation of the magnesium as the oxyquinoline.

A general method for the determination of mercury in various types of pharmaceutical preparations is proposed by Rotandaro (*169*). This involves a modification of the ethanolamine-reduction method of Rauscher (*164*) by adding zinc dust and forming a mercury-zinc amalgam. This procedure appears to give rapid and accurate determinations as it is applied to a large majority of mercurial preparations and has received official recognition by the U. S. Pharmacopoeia XIII. For mercury in toxicological material Elmore (*60*) has proposed a wet oxidation procedure which involves refluxing with sulfuric and fuming nitric acids and subsequent extraction with dithizone. This procedure shows some promise in the assay of medicinal products containing mercury. Still another method having good prospects in the determination of mercury in pharmaceutical preparations is proposed by Gentry and Sherrington (*74*), who also discuss probable interferences from other elements. In this method the mercury is precipitated as mercuric iodate which is subsequently determined either volumetrically or gravimetrically.

A microadaptation of the U.S.P. method for the determination of silver salts is discussed by Brown and Waller (*31*), who also report that the application of the hydrofluoric acid–sulfuric acid treatment to the U.S.P. assay for protein silver compounds yields theoretical results. Calamine lotion may be analyzed for total zinc oxide by a procedure suggested by Wilson and Sperling (*214*), who have also indicated that a method is available for determining the quantity of bentonite and ferric oxide in the same preparation.

VITAMINS

The ability of ascorbic acid to reduce the dye 2,6-dichlorophenolindophenol has been the basis for the development of chemical methods for the determination of this vitamin (*23, 95, 194*). Titrimetric procedures in acetic-metaphosphoric acid (*146*) and in oxalic acid (*78*) solution have high specificity. Iodometric titrations are useful in relatively pure systems and both visual and electrometric (*1*) methods have been reported.

What is described as a simple and accurate gravimetric procedure for the assay of choline chloride in pharmaceutical products, proposed by Gakenheimer and· Reguera (*73*), involves precipitation of the choline as choline phosphotungstate from an anhydrous alcohol solution.

For relatively pure systems of vitamin K oxidation-reduction methods involving 2,6-dichlorophenolindophenol titration of the reduced quinone are reported (*196*). Reduction with zinc and titration of the reduced quinone with ceric sulfate is the accepted U.S.P. method (*197*). Because most pharmaceutical preparations having vitamin K activity contain 2-methyl-1,4-naphthoquinone (menadione) as the active ingredient, the analytical procedures for this compound can thus be made simpler than those for natural products which could contain vitamin K_1 or K_2, or both. The addition of potassium iodide to an acid-alcohol solution of 2-methyl-1,4-napthoquinone and the titration of the liberated iodine with sodium thiosulfate has been described (*220*). Schoen (*173*) has suggested a modification of the U.S.P. XII method for the determination of menadione sodium bisulfite which liberates the menadione from the water solution by the addition of sodium hydroxide. The liberated menadione is then extracted by ether and determined gravimetrically.

Tocopherols may be assayed by mild or vigorous oxidation (*25*), the specificity of which is increased by catalytic reduction of interfering carotenoids. Quantitative recovery of α-tocopherol in chromatographic methods appears unlikely, as other tocopherols are not removed. For the estimation of γ-tocopherol diazotization appears to be the best procedure.

GENERAL

Martin *et al.* (*135*) have studied the determination of some of the official aldehydes using both the volumetric oxine methods and gravimetric methods using 2,4-dinitrophenylhydrazine. They studied benzaldehyde, cinnamaldehyde, and vanillin, with vanillin serving as the reference, and made a check assay by the methoxy method. They conclude that the volumetric method appears most suitable for benzaldehyde and cinnamaldehyde. Total aldehydes in oil of cinnamon have been determined by Darlington and Christensen (*51*) who utilized a sulfite-bisulfite method.

Smith *et al.* (*179*) describe a method for determining aloin in aloe by the use of immiscible solvents, and Poe and Holtquist (*162*) after studying three possible assay procedures for aromatic spirit of ammonia conclude that the present assay methods are adequate. The determination of benzoic and salicylic acids in compound ointment of benzoic acid is discussed by Kenike (*119*). This involves the total titration of both acids with standardized alkali and the extraction of the benzoic acid with ether at the phenolphthalein end point.

Jensen and Jannke (*109*) have adapted the method of Khait to the determination of 3-chlorobutanol by decomposing with 0.5 N alcoholic potassium hydroxide and titrating the excess potassium hydroxide with 0.5 N hydrochloric acid, substituting methyl orange for phenolphthalein as the indicator in order to include in the titration any potassium carbonate formed during decomposition. In order to determine chlorobutanol in oil, the sample is digested with a solution of potassium hydroxide and calcium hydroxide in the presence of Fehling's solution as an oxidizing agent. It is then distilled into water and cooled by a freezing mixture, sodium hydroxide is added along with an excess

of 0.1 N iodine, and the excess of iodine is titrated with 0.1 N sodium thiosulfate after acidification. Good recoveries are reported.

Evidence is presented by Goldstein (*83*) to indicate that the distillation method of the U.S.P. XII for the determination of chloroform is the method of choice when it is compared with a modified Volhard procedure and a modified Randall procedure which salts out the chloroform and measures it directly.

According to Wessel *et al.* (*205*) glycerol may be determined in the presence of large quantities of gelatin by precipitating the gelatin with sodium tungstate and determining the glycerol in the filtrate by the A.O.A.C. method.

The micro-Kjeldahl determination of gramicidin and tryptophan has been studied by White and Secore (*207*). They conclude from the comparison of the Gunning-Arnold-Dyer and Frederick methods that mercuric oxide is a suitable catalyst. A specially designed trap has been utilized by Jonnard (*110*) for the determination of nitrogen in proteins and their hydrolyzates by a semimicro-Kjeldahl method.

A critical review of the official tests for heavy metals as described in the U.S.P. XII has been made by Bundy and Edman (*35*). They list a summary of the limiting factors for the prescribed tests.

Deichmann (*55*) has modified the reagents of Melzer, Millon, Liebermann, Guareschi, and Cotton to permit the qualitative differentiation of *o*-, *m*-, and *p*-cresols. The quantitative determinations of progesterone in oil by precipitating with 2,4-dinitrophenylhydrazine is reported by Klein *et al.* (*124*). In this reaction 1 mole of progesterone reacts with 2 moles of reagent.

According to Green (*88*) sodium acetate, sodium benzoate, sodium salicylate, sodium phenobarbital, and sodium sulfathiazole can be estimated in a nonaqueous medium by titrating with 0.1 N to 0.5 N perchloric acid in a mixture of propylene glycol and isopropyl alcohol, using indicator dyes and potentiometers to determine the end point. Sodium pentobarbital gave low results with the potentiometer but good results when an indicator was used. Pentobarbital gave relatively low results by all methods; sodium sulfadiazine can not be titrated in this manner, at least not without considerable modification of this method.

A titrimetric method has been proposed by Rosenblum and Mildworm (*168*) for the determination of saccharin after it has been extracted from diluents with a mixture of chloroform and ether. The Karl Fischer reagent has been adapted to a microscale determination of water by Levy *et al.* (*130*) and the evaluation of official and unofficial species by psyllium and their mucilages has been studied by Greenberg (*90*). This author recommends a convenient method for the quantitative determination of the mucilage. He has also studied two native unofficial plantago seeds and compares them with those now official.

PHYSICOCHEMICAL METHODS

ALKALOIDS AND RELATED SUBSTANCES

A colorimetric procedure for the determination of acetophenetidin is proposed by Degner and Johnson (*54*) which involves acid hydrolysis followed by treatment with chromic acid to form a highly colored compound that can be determined photometrically. Haley (*94*) reports that benadryl and pyribenzamine hydrochloride may be identified by using chloroplatinic acid which gives distinctly different color reactions with the two compounds, and Keenan has described the optical crystallographic properties of benadryl and pyribenzamine (*113*) together with significant microchemical reactions with platinic chloride reagent. He reports a similar study for demerol (*112*), for hydrastis and its principal alkaloids, hydrastine and berberine (*114*), and together with Warren (*118*), has described the crystallographic data which serve to differentiate the four principal alkaloids of cinchona—quinine, quinidine, cinchonine, and cinchonidine.

The adaptation of the method of Bratton and Marshall (30) for the determination of sulfonamide derivatives to the colorimetric determination of local anesthetic agents is discussed by Bandelin and Kemp (11). Benzocaine, procaine hydrochloride, butacaine sulfate, and butyl aminobenzoate give positive tests while sulfonamides interfere. No interference was encountered with cocaine, metycaine, alpine, stovain, diathane, nupercaine, and phenacaine.

Conn (44) has published an amperometric titration procedure which is based on the formation of insoluble diamidine alizarin sulfonates and permits rapid and quantitative estimation of certain diamidines alone or in simple pharmaceutical preparations.

Warren et al. (200) describe a colorimetric method in which sodium-β-naphthoquinone-4-sulfonate (purified) reacts with digitoxin in alkaline solution to form a purple color. The addition of acetic acid to the purple color changes it to yellow and stabilizes it. The Kiliani reaction of digitoxin has been studied by James et al. (107). The blue color which is developed with glacial acetic acid containing a trace of ferric chloride and sulfuric acid is the basis for a proposed colorimetric method for the assay of digitoxin which would utilize a standard powder as a reference sample.

A collaborative study of the assay of digitalis and its preparations by the chemical and cat methods is discussed by Bell and Krantz (18) The chemical method (20) which is based on the colorimetric assay of the active glycosides by means of the Baljet color reaction is compared to the cat method. In another paper these same authors (19) recommend a revision of the U.S.P. control procedure for the assay of digitoxin so as to use tetraethyl ammonium hydroxide as the alkali. This revision greatly improves the Baljet spot testing for cardiotonic glycosides. Anderson and Chen (5) have also proposed a colorimetric assay for digitoxin which depends upon the blue color formed when digitoxin is treated with a dilute solution of m-nitrobenzene and sodium hydroxide. The color is not specific for digitoxin but serves as a quantitative measure if other cardiac glycosides are not present. A comparison of the U.S.P. cat method and the proposed method is given. Swoap's (192) comparison of the Knudson-Dresbach colorimetric procedure and the cat method for the estimation of digitalis appears to emphasize the need for a different standard for each type of digitalis preparation, while Goldstein (85) gives a general discussion and reports the results he has obtained when applying the Knudson-Dresbach colorimetric method as modified by Bell and Krantz to the assay of digitalis.

Grove and Vos (92) have described a method for extracting ergonovine from ergot and estimating it colorimetrically with p-dimethylaminobenzaldehyde. A collaborative study of the assay of ergot extending over a period of several years is discussed by Smith (180). A colorimetric method is recommended by which ergot and ergot preparations are assayed for total alkaloids and for ergonovine.

β-Erythroidine may be determined colorimetrically by a method suggested by Dietz and Folkers (57) which involves treating the alkaloid with strong sulfuric acid to form a degradation product which gives an intense purple color with ferric chloride solution.

Bandelin (10) has described a colorimetric procedure for the determination of homatropine methyl bromide which precipitates the alkaloid as the insoluble reineckate with ammonium reineckate. The precipitate is filtered off, washed, dissolved in acetone, and then determined spectrophotometrically at 525 mμ. The extraction procedure and interfering substances are discussed. A procedure for the assay of solanaceous drugs and some of their preparations, described by Brown et al. (33), makes use of the principles of selective absorption and when compared with official methods gives more precise and accurate results and requires less time.

A method for the colorimetric determination of penicillin, which is described by Staab, Ragan, and Binkley (186) and later revised by Ford (69), is based upon the fact that penicillin reacts rapidly with hydroxylamine to give a hydroxamic acid which forms a purple complex with ferric ion.

Spectrophotometric procedures for the determination of streptomycin have been developed by Boxer, Jelinek, and Leghorn (29). One procedure was suggested by the observation that streptomycin on being heated with dilute alkali forms maltol, which shows characteristic absorption maxima in the ultraviolet in both acid and alkaline solutions and reacts with ferric ions to give a purple-red color. They also observed that maltol reacts with a phenol reagent of Folin and Ciocalteu to give the usual blue color. A fluorometric method has been described by Boxer and Jelinek (28) which is dependent on the aldehyde group and the strong basic character of the streptomycin molecule. This method is very sensitive and is recommended for the determination of streptomycin in blood.

CHEMOTHERAPEUTIC AGENTS

Application of the immersion method for the microscopic identification of the crystalline sulfonamides is reported by Keenan (115). He lists the optical crystographic data for six sulfonamides, microchemical tests, and optical constants for crystalline complexes formed with specific reagents. Other identification tests for sulfonamides involving colored solutions and reagents with copper and cobalt salts are described by Sample (170), who also lists tables giving the various colors formed at specfic time intervals.

METALLIC IONS AND RELATED SUBSTANCES

Photometric measurement of the hydroxyquinolate of aluminum after extraction with chloroform is recommended by Gentry and Sherrington (75) who also suggest the possibility of a fluorometric method for the same compound due to an intense greenish yellow fluorescence which accompanies absorption of violet light by the chloroform solution. Good recoveries of known amounts of aluminum are reported.

A scheme of analysis is reported by Stafford et al. (187) for the successive determination of minute amounts of copper, arsenic, lead, zinc, and iron in a 2-gram sample of organic material—i.e., medicinals. It has been devised principally for application to compounds with a very low metal specification; however, it is sufficiently flexible to be adapted to materials with a somewhat higher metal content. Under the given conditions the method is found to be specific for arsenic, lead, and iron. Bismuth will interfere with the determination of copper and cadmium is included with zinc. Conditions are described for eliminating these interferences and determining bismuth, nickel, and cadmium, if desired. Another colorimetric determination for bismuth in pharmaceutical preparations and biological material which makes use of the relatively stable yellow color of the complex formed when thiourea reacts with bismuth has been described by Cronheim and Wright (49).

Colorimetric methods for the determination of iron which might possibly be used in the pharmaceutical field are described by Bandemer and Schaible (12) and Yoe and Jones (218). The procedure suggested by Yoe and Jones may be carried out in the presence of fluorides, phosphates, tartrates, citrates, oxalates, etc. Detailed procedures are given for the use of the reagent which is disodium 1,2-dihydroxybenzene-3,5-disulfonate.

Steinmetz and Green (188) have published what is claimed to be a rapid and reliable procedure for the determination of lead in pharmaceutical preparations by the dithizone method. Cholak et al. (42) have also described a method for the determination of lead in biological material, which is dependent upon the extraction of the lead at a high pH. The extraction step is incorporated

in the final estimation step of the Bambach-Burkey method. Difficulties and advantages of the revised method are discussed and analytical data given to prove the adequate nature of the revision.

Phosphorus may be determined colorimetrically in a large number of preparations including pharmaceuticals as molybdivanadophosphoric acid. Kitson and Mellon (122) have studied the effects of the following variables in this procedure: acidity, reagent and phosphorus concentration, temperature, order of adding reagents, stability, and effects of some 60 diverse ions.

VITAMINS

The procedure first described by Carr and Price (41) involving the reaction between natural vitamin A and antimony trichloride has been the basis of the physicochemical methods having the widest applicability for the determination of vitamin A. Theories concerning the mechanism of the reaction together with some ideas of the structures required to produce the color have recently been published (140, 141). Newer procedures include the development of a new color reaction for vitamin A by Sobel and Werbin, utilizing practical (185) and activated (183) glycerol 1,3-dichlorohydrin (made by codistillation of antimony trichloride and glycerol dichlorohydrin in vacuo) for vitamin A in fresh liver oils (184) and serum (182). This reagent has the advantages of longer stability of color (2 to 10 minutes), nonsensitivity to traces of moisture, and noncorrosiveness. On the other hand, its $E_{1cm.}^{1\%}$ (or $L_{1cm.}^{1\%}$) values are only approximately one fourth those of the Carr-Price color and the interference of β-carotene is approximately twice as great as in the Carr-Price reaction. The greater time of stability of the color with activated glycerol dichlorohydrin permits the use of null-point instruments, such as the Beckman spectrophotometer. In the Beckman and similar instruments increased cell lengths also permit increases in optical density to compensate for the low absorption-concentration ratio.

Peters' (156) discovery that thiamine can be oxidized in solution to a substance exhibiting a blue fluorescence (thiochrome) has received widespread attention. Jansen (108) has proposed a quantitative fluorometric method for the estimation of thiamine based on this phenomenon. Although the yield of thiochrome from thiamine is not quantitative (45), it is consistent under rigidly controlled conditions and most present methods utilize thiochrome fluorescence as a means for estimating vitamin B_1. Comparison of the U.S.P. XIII and other methods for vitamin B_1 is presented by Williams et al. (212) and Elvidge (62).

Enzymatic hydrolysis and purification by adsorption and elution are generally not necessary in preparations containing relatively high concentrations of thiamine or lower concentrations of synthetic vitamin B_1. However, in mixtures containing the thiamine in bound form—viz., the phosphoric acid esters—preliminary enzymatic hydrolysis will increase the results appreciably. In this type of preparation nonspecific fluorescence cannot always be compensated for by the use of a blank, so that adsorption or base exchange and elution with an activated zeolite or similar column may be necessary as a purification step.

Colorimetric methods based on the coupling of thiamine with a diazonium salt have been reported by Kinnersley and Peters (120), Prebluda and McCollum (163), and Melnick and Field (137), among others. Polarographic methods have also been reported (62, 171) but difficulties due to evolution of hydrogen from the buffer acid partly masked the diffusion current obtained. These colorimetric and polarographic methods are considerably less specific in their reactions than the thiochrome procedure and, in general, less dependence on isolation and purification steps is necessary with the thiochrome method. The precise control of conditions makes the thiochrome method somewhat tedious; however, the increased specificity and sensitivity and fewer purification steps tend to compensate for this disadvantage.

When riboflavin is activated by high frequency visible light (425 to 475 mμ) it fluoresces, emitting greenish-yellow visible light, having an emission spectrum with a maximum at about 565 mμ. Hodson and Norris (103), Conner and Straub (46), and Arnold (6) have utilized this property to develop fluorometric methods for the estimation of this vitamin. Variations in the procedures have been confined largely to methods for the elimination of interfering substances by oxidation, reduction, adsorption, or combinations of these. Sodium dithionite and stannous chloride solutions have been used simultaneously (103) to reduce both riboflavin and certain interfering substances. The riboflavin which is reversibly reduced can be regenerated by shaking in the presence of air, while the impurities remain in a reduced form. The difference between the readings before and after the addition of sodium hydrosulfite (68) is considered to be the fluorescence due to riboflavin and is the basis for a simpler procedure for the estimation of this vitamin. Interfering pigments (6) may be removed by oxidation of the sample with dilute potassium permanganate and the removal of excess potassium permanganate with hydrogen peroxide. This oxidation must be performed in acid medium to prevent clouding of the solution and the oxidized sample is then buffered to a pH of 6.0 to 7.0 for maximum fluorescence (126). Riboflavin may also be separated from interfering components (46, 68) by adsorption on certain fuller's earth preparations and subsequent elution with pyridine-acetic acid solution.

Bessey (22) has suggested a colorimetric procedure for ascorbic acid estimation in which the excess dye in a standard aliquot of indophenol reagent is extracted with xylene and the xylene solution of the dye is measured in a photoelectric colorimeter. This method offers greater freedom from interfering pigments by permitting the use of a blank.

A solution of the derivative resulting from the reaction between ascorbic acid and 2,4-dinitrophenylhydrazine in 85% sulfuric acid has been used by Roe and Kuether (166) for the colorimetric determination of total ascorbic acid—the color developed is indicative of both ascorbic and dehydroascorbic acid and can be measured quantitatively in a suitable photoelectric colorimeter or spectrophotometer.

Differential procedures for the estimation of ascorbic acid, dehydroascorbic acid, and diketogulonic acid utilizing the 2,4-dinitrophenylhydrazine method have recently been described (167). The estimation of ascorbic acid content of a substance may not necessarily indicate the entire physiological vitamin C activity of the substance, for there is still considerable question concerning the oxidation products of ascorbic acid, both as to structure and physiological activity.

Dichlorophenolindophenol (175), dinitrophenylhydrazine (153), and cyanoacetic acid (158) have all been used as reagents for the development of colorimetric methods for the estimation of vitamin K, both synthetic (2-methyl-1,4-naphthoquinone) and natural.

Colorimetric methods for the determination of nicotinamide (niacinamide) and nicotinic acid have been based, in general, on the reaction proposed by König (125) and Zinke (221) of pyridines having no substituents at either alpha- position with cyanogen bromide and an aromatic amine. Both nicotinic acid and nicotinamide react to produce a transient yellow color, but the reaction rates and maximal intensities of equivalent quantities of the two compounds differ (127, 138).

Lamb (127) and Melnick and Oser (138) have developed differential methods of analysis for nicotinamide and nicotinic acid in the same sample, but the deviation in duplicate samples may be as high as ±10 to 15%. This type of differential method has a definite value in that microbiological methods for the estimation of this vitamin do not differentiate between nicotinic acid and nicotinamide.

Mueller and Fox (145) have recently proposed another improvement in the method in which the sample is hydrolyzed in

order to obtain all the vitamin in the acid form. Ammonia is used in place of the aromatic amine and the final reaction mixture is buffered to provide a better pH control. The sensitivity of the method is increased considerably, and this permits greater dilution of interfering substances.

Goodyear and Murphy (86) have described a colorimetric method involving the hypobromite degradation of the nicotinamide to 3-aminopyridine. The amine is subsequently diazotized and coupled with sodium β-naphtholate to form a characteristic dye, the absorption of which can be measured photoelectrically.

Wilson et al. (215) have determined hesperidin and other flavones of quercetin by a borocitric acid method which produces a yellow color, the optical density of which is a quantitative measure of the flavone. Davis (53) has suggested the use of alkaline diethylene glycol to form yellow compounds with flavones which are allowed to develop for 5 minutes. These are not intended for specific procedures but offer a suitable means of evaluating the general quercetin content of foods and pharmaceuticals. Ferric chloride in methanol may also be considered as a reagent for these quercetin derivatives. Fluorometry of boric acid compounds has also been tried by Glazko et al. (79).

The formation of an insoluble complex with Reinecke's salt appears to be the preferred chemical method for the determination of choline (25, 65, 80, 132). This forms a colored complex in acetone and the concentration may be determined in a suitable colorimeter.

Hutchings et al. (106) have proposed a method for folic acid which involves reduction, diazotization, and coupling with a suitable amine which appears to have preference over ultraviolet absorption which has been used for its estimation. The color thus formed can be examined in a suitable colorimeter. Bloom et al. (27) have further discussed the assay of folic acid.

The Emmerie-Engel (64) colorimetric method has been used for a number of years to determine total tocopherols and its simplicity and sensitivity appear to ensure its continued use in most laboratories. Hines and Mattill (102) give further information on the assay of tocopherol.

Platt and Glock (159) have proposed an oxidation procedure for the assay of inositol which involves oxidation at a low temperature (6° to 8° C.) with iodate and preliminary purification by ion exchange before the reaction is carried out. General information on the assay of inositol is presented by Wooley (217).

The colorimetric methods described by Scudi et al. (176–178), which employ a barbituric acid buffer and the coupling agent 2,6-dichloroquinone chloroimide, are satisfactory for the estimation of pyridoxine in some mixtures of the B complex family. Chromatography offers some promise for purification but ideal conditions remain to be worked out. As in some other physicochemical tests for vitamins one must rely on an animal or microbiological assay for specificity of the applied procedure. The utilization of microbiological verification is extremely important when impurities react in the same physicochemical manner as the vitamin under test. For this reason, several approaches to the selection of a method should be tried. Another colorimetric method which involves the use of diazotized sulfanilic acid and phenol reagent has been suggested by Swaminathan (191) for pyridoxine. This is not as specific as the preceding methods. Brown et al. (32) have suggested the use of p-aminoacetophenone as a coupler for the determination of pyridoxine hydrochloride and Lingane and Davis (131) have also discussed the polarographic analysis of this vitamin.

Vitamin D may be assayed according to the method of Nield et al. (152) which involves the action of acetyl chloride and antimony trichloride when vitamin A is absent. Sobel et al. (181) have recently proposed a procedure which employs glycerol dichlorohydrin in the presence of acetyl chloride for its colorimetric estimation. Young (219) and DeWitt and Sullivan (56) have suggested the use of chromatography for the separation of vitamin D from vitamin A, which then could be followed by one

of the above-mentioned color developers or direct absorption spectroscopy for the evaluation of the vitamin D content. Milas et al. (142) and Nakamiya and Koizumi (150) have suggested spectroscopic methods which involve the removal of any vitamin A by irradiation before determining the extinction coefficient of vitamin D. The determination of vitamin D is discussed at length in Biological Symposia (25).

The Eastern Regional Research Laboratories (58) have suggested spectrophotometric methods of analysis of rutin with respect to rutin, quercetin, red pigment, and chlorophyll content. Because rutin can be readily isolated in relatively pure form from natural sources, one may easily determine the above constituents. Spectral transmission curves in the region 400 to 700 millimicrons and also in the ultraviolet range of 240 to 400 millimicrons establish the wave length necessary to determine each material. Glazko et al. (79) have used fluorometry to estimate rutin content. Naghski et al. (147) also discuss the analysis of rutin.

Tauber and Laufer (193) have developed a colorimetric method for p-aminobenzoic acid, which depends on the formation of a yellow color with p-dimethylaminobenzaldehyde, while Kirch and Bergeim (121) have suggested the reaction of p-aminobenzoic acid with diazotized thiamine as a basis for a quantitative measurement. Ekstrand and Sjogren (59) have also discussed the assay of p-aminobenzoic acid.

Scudi (174) has proposed a fluorometric method for the determination of nicotinamide based on the work of Najjar and others (148, 149) on the identification and determination of N^1-methylnicotinamide. In this procedure the N^1-methyl derivative is formed with methyl iodide, treated with alkali, and extracted with isobutyl alcohol. The isobutyl alcohol extract exhibits a bluish fluorescence which bears a quantitative relationship to the concentration of nicotinamide in the sample.

Friedemann and Frazier (71) and Scudi (174) have also described a fluorometric procedure based on the formation of fluorescent derivatives of nicotinamide with cyanogen bromide solution.

GENERAL

Peterson and Harvey (157) have proposed a quantitative colorimetric method for the estimation of pure ergosterol which is the reversed Salkowski reaction, using concentrated sulfuric acid on a carbon tetrachloride solution of the sample. The separation and quantitative determination of ergosterol, cholesterol, and 7-dehydrocholesterol are proposed by Lamb et al. (128) by measurement of the optical density of the characteristic absorption maxima of the reaction products resulting from the treatment of the chloroform solution of these sterols with an antimony trichloride–acetyl chloride reagent.

Carol and Molitor (37) have modified the Kober method for the determination of α- and β-estradiol. Their method is based on the fact that β-estradiol reacts with Kober's reagent in the cold while α-estradiol does not. Results of the analysis of a series of samples containing the two isomers are given. Gottlieb (87) proposes a nitrosophenol quinoid procedure for the analysis of diethylstilbestrol in pharmaceutical and cosmetic preparations Carol and Rotandaro (39) have proposed a procedure for the determination of estrone in oil solutions of estrogens which depends upon the extraction of the estrogens by immiscible solvents, then the separation of the ketone fraction with Girard reagent T followed by spectrophotometric determination of estrone.

A colorimetric method for the determination of gallic acid which has been added to fats and oils is recommended by Mattil and Filer (136). This method utilizes a ferrous tartrate reagent to form the color. For the estimation of gentian violet McIntyre and James (133) recommend a colorimetric method in which a standard reference powder is used for evaluation purposes.

Details of an alkali-isomerization and subsequent spectroscopic techniques are given by Hilditch et al. (99) for the determination of linoleic, linolenic, and eleostearic acids.

Bryant et al. (34) report 95 to 100% recovery of pectin in biological material by converting it to pentose, which in turn produces furfural which may be measured photometrically. In another approach to the estimation of pectin Williams and Johnson (213) state that 5 to 50 mg. of pectin or pectic acid may be determined by electrodeposition with the same order of accuracy as that obtained in the calcium pectate method and in much less time.

A simple and accurate method for the determination of peroxides in mineral oil, reported by Golden (82), depends upon the oxidation of ferrous ion to ferric ion with subsequent development of a pink or red color. It is reported that this test may be used for the determination of peroxides in other oils, such as cod liver oil or vegetable oils, and may be applied to the evaluation of the effectiveness of antioxidants.

A spectrophotometric method for the determination of phenolphthalein in mineral oil emulsions has been proposed by Frederick and Koff (70). The color produced in alkaline solution is used as a basis for the assay and the relation between the per cent transmission of light at 550 mμ and the concentration of phenolphthalein is given.

Klein (123) reports that microquantities of sulfates may be determined by first precipitating as benzidine sulfate and then coupling with Marshall's (30) reagent. The color produced is read in a photoelectric colorimeter. According to Carpenter (40) the absorption spectra of the blue color produced in the tryptophan–glyoxylic acid reaction have three distinct absorption regions and may be adapted to a quantitative estimation of tryptophan.

PHYSICAL METHODS

ALKALOIDS AND RELATED SUBSTANCES

Systematized procedures based on differences in solubilities in various solvents are proposed by Wilson and Hilty (216) for the separation and determination of medicinal preparations in which caffeine is in combination with one or more of the following agents: acetylsalicylic acid, phenacetin, codeine, acetanilide, quinine, sodium bicarbonate, sodium bromide, or aminopyrine. The same authors (101) have proposed procedures for the separation and determination of mixtures of medicinal compounds in which an ephedrine salt is in combination with one or more of the following: barbiturates, acetylsalicylic acid, phenacetin, and aminophylline. Holt (104) has separated caffeine·from acetylsalicylic acid and acetophenetidin by extraction with ether. Acetylsalicylic acid is then separated from the acetophenetidin by extracting the ethereal solution with sodium bicarbonate. The same investigator (105) developed further the separation of caffeine from the following substances: ephedrine, acetanilide, camphor, monobromated camphor, phenobarbital, and aspirin.

Trautner and Roberts (195) have described a method for the separation of hyoscine and hyoscyamine in which both alkaloids are adsorbed from a benzene solution by silica. Hyoscine is rapidly eluted by absolute alcohol while hyoscyamine is moved only slightly. By making use of this principle the two alkaloids can be separated almost quantitatively so long as the hyoscine-hyoscyamine ratio lies between 1 to 4 and 6 to 1.

In a report of the combined Pharmaceutical Contact Committee of the American Drug Manufacturers Association and the American Pharmaceutical Manufacturers Association, Copley (48) recommends a revised procedure for determining melting points of cocoa butter.

ANTIBIOTICS

Grenfell et al. (91) described a polarimetric method for the determination of penicillin. This method is rapid and simple but cannot be used on fermentation broths and material of low potency. The same authors have also suggested a spectrophotometric method for the determination of penicillin G by utilizing

the slightly different ultraviolet absorption properties of penicillin G in relation to the other penicillins. This method, like the polarimetric method, is not applicable for use on fermentation broths or material of low potency.

Barnes et al. (14) have discussed at length the qualitative infrared spectra of crystalline sodium penicillins G, F, X, K, and amyl. They list a suitable analytical infrared absorption frequency and have given a procedure for the analysis of sodium penicillin G.

CHEMOTHERAPEUTIC AGENTS

In a paper presenting the ultraviolet absorption spectra of seventeen sulfonamides in distilled water Ciminera and Wilcox (43) suggest a quantitative method for the determination of sulfonamides in pure solution.

VITAMINS

Morton and Heilbron (144) first observed that ultraviolet absorption of certain fish liver oils at 328 mμ was proportional to the color developed with the Carr-Price reagent for vitamin A. Various procedures have since been developed utilizing the ultraviolet absorption spectrum of vitamin A for its estimation. The preparation of vitamin A-free blanks by chromatographic adsorption has recently received the attention of Awapara et al. (8) as a means of improving ultraviolet absorption procedures. Wilkie (210) has reviewed the results of collaborative assays both on the ultraviolet absorption and the Carr-Price methods.

Lingane and Davis (131) have described a polarographic method for the estimation of riboflavin in a phosphate buffer at pH 7.2, but the method apparently has not received further study. The same authors (131) have applied polarographic techniques to vitamin mixtures, yielding the information that nicotinic acid exhibits a wave in tetramethylammonium borate buffer (pH 9.0). The half-wave potential is −1.6 volts vs. the saturated calomel half-cell.

Relatively pure concentrates of vitamin K can be estimated by means of ultraviolet absorption measurement as reported by Dam (50). The absorption curves for vitamins K_1 and K_2 have been reported by Ewing et al. (66) and Hershberg et al. (97) have described a method that involves polarographic estimation of the vitamin.

Frost (72) has suggested an optical rotation method for the assay of pantothenic acid when pure systems are encountered and Lingane and Davis (131) have studied the use of the polarograph in the analysis of this vitamin. The resistance of the molecule prevents, to a great extent, the chemical determination, so that microbiological procedures appear to be the best means of evaluating it when it is found in mixtures with other constituents. Willerton and Cromwell (211) have suggested the use of enzyme clarase and Buskirk and Delor (36), the enzyme mylase-p, to prepare natural materials before assay.

When pure systems of vitamin B_6 (pyridoxine hydrochloride) occur, the method of choice is the direct ultraviolet spectrophotometric procedure described by Miller (143) which utilizes the 292 mμ region. The pH of the aqueous solution must be rigidly controlled, as this vitamin will shift spectral positions with pH change.

GENERAL

A simple, rapid, and accurate polarographic method for the determination of acetaldehyde in mixtures of alcohol is reported by Elving and Rutner (63). By diluting acetone with 2,2,4-trimethylpentane Barthauer et al. (15) have been able to determine the optical density at 280 mμ. A method in which formaldehyde may be determined polarographically in the presence of acrolein and other aldehydes is reported by Whitnack and Moshier (208).

The estimation of aloins and aloe-emetine by polarographic

procedure is outlined by Stone and Furman (*190*) and Stone (*189*), while the dropping mercury electrode has been the means used for determining copper in copper proteins by Ames and Dawson (*3*).

The estimation of camphor and alcohol in spirit of camphor is accomplished by Plein and Poe (*160*) by determining the refractive index and specific gravity of the solution and referring to a preconstructed chart made from known concentrations of the ingredients. These same authors (*161*) have also estimated camphor and alcohol by determining the optical rotation and specific gravity.

The isolation of trihydroxymethylanthroquinones of cascara on chromatographic columns and subsequent elution and spectrophotometric determinations of optical densities have been proposed by Gibson and Schwarting (*76*) for the analysis of cascara preparations. Gibson *et al.* (*77*) have found that under a given set of conditions the three isomers separate into three distinct bands on the chromatographic tube. This isolation in conjunction with spectrophotometry is used as a basis for a method of quantitative analysis of cascara.

What is claimed to be a simple spectrophotometric procedure for the estimation of dihydroxyanthranol and dihydroxyanthraquinone, individually or in admixtures, is described by Auerbach (*7*). Goetz and Seif (*81*) have adapted the spectrophotometric method of Elvidge (*61*) to the practical control of hexestrol and its pharmaceutical preparations.

A method is described by Carol *et al.* (*38*) for the determination of the estrone equilin and equilenin in mixtures by infrared spectrophotometry. Optical density measurements are made at a selected absorption peak and from these data a concentration of each ketosteroid is determined by a graphical approximation method.

The optical rotation of methyltestosterone is used as a basis for the official U.S.P. (*198*) assay. This monograph also recognizes an ultraviolet absorption band for identification purposes which might possibly be utilized as another means of analysis.

Gallic acid which has been added to fats and oils as an antioxidant may be determined spectrophotometrically by measuring its spectral absorption at 270 to 271 mμ in a manner described by Mattil and Filer (*136*). Daubert (*52*) has employed both spectrographic and spectrophotometric methods of analysis in determining quantitatively the linoleic, linolenic, and, in a few instances, arachidonic acid content.

The percentages of ethanol and methanol in mixtures of the two have been determined by Beyer and Reeves (*24*) by determining the specific gravity at 15.56° C. and the respective Zeiss immersion refractometer readings at 17.5° and 20.0° C.

Watson (*203*) has used the electron microscope to determine particle size; in a general discussion he sets forth technique and procedures that constitute a useful working set of instructions.

Robinson and Werch (*165*) have determined camphor in solution with phenol and a high percentage of light mineral oil by first emulsifying a weighed sample with 95% ethyl alcohol and then centrifuging and separating the alcoholic extract of camphor. Good recoveries are reported.

Keenan and Eisenberg (*117*) have compiled data on the microscopic identification of crystalline substances receiving official recognition in the National Formulary VII.

Three procedures are proposed by Bennett (*21*) for separating mixtures of substances that differ in their solubility in a given solvent but in which none are insoluble. The underlying principle of these methods is that a substance does not dissolve in a solvent already saturated with it. Of the three methods discussed, the second has given the most accurate results but requires exact knowledge of the components present. This method involves the extraction of one component from an *N*-component mixture by using a solvent saturated with all the ($n-1$) other components.

Many other methods of analysis have undoubtedly been investigated and found useful in the pharmaceutical field. In the

assay of vitamins alone, particularly good reviews of the various methods are available in the twelfth volume of *Biological Symposia* (*25*) and in "Methods of Vitamin Analysis" (*139*). Chromatography, infrared absorption, flame photometry, x-ray diffraction, and nephelometric and turbidimetric procedures and techniques have all been tried and found useful. The immediate future of all these newer analytical approaches to practical analytical methods of analysis in the pharmaceutical and natural drug field seems assured as the conditions affecting their utilization are more extensively revealed.

ACKNOWLEDGMENT

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Natural and Synthetic Rubbers

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THIS paper is the first of a series of annual reviews on analytical methods pertaining to natural and synthetic rubbers. It covers the period from 1944 to the present, in order to include practically all the publications in the relatively new field of synthetic rubber. Articles appearing earlier than 1944 are mentioned only if they are very special ones or refer to some classical procedure. On the other hand there have been omitted from this review methods for the analysis of compounding ingredients and of raw materials used in the manufacture of synthetic rubbers, as well as physical tests applied to rubber vulcanizates and such physical tests on raw polymers as molecular weight determinations, sol-gel ratios, viscosities, and swelling. It has been necessary to restrict the review to new methods that have been applied successfully in the analysis of rubbers.

GENERAL

In most countries there are standard procedures for the chemical analysis of rubbers and rubber products. In the United States three groups promulgate such standards, (1) Committee D-11 on Rubber and Rubberlike Materials of the American Society for Testing Materials (A.S.T.M.), (2) Federal Specification Board, and (3) Office of Rubber Reserve of the Reconstruction Finance Corporation (Rubber Reserve). The A.S.T.M. pub-

lishes the latest revisions of its methods annually. Methods of the A.S.T.M. for the chemical analysis of rubber products (7) have not changed since 1943, but in 1946 there was added a method (8) for the identification and quantitative analysis of synthetic rubbers. An A.S.T.M. method on natural latex will soon appear. The latest revision of the federal specification (216) on methods of test for rubber goods, promulgated in 1940, is out of date. It is now being revised to include methods on synthetic rubber products and should be issued sometime in 1949. The specifications for government synthetic rubbers (156) include methods for the chemical analysis of synthetic rubbers and latices made in government plants.

In England the British Standards Institution in 1940 published methods for the testing of latex and crude rubber (44) and vulcanized products (45). It is understood that both publications will appear soon in extensively revised and enlarged form. In France the Association Française de Normalisation (17) and in Germany the Deutscher Verband für die Materialprüfungen der Technik (64) promulgate methods for the chemical analysis of rubber. Other countries also have similar organizations. Basically, the chemical methods are in most cases the same in all countries.

Summaries or abstracts of articles on the chemical analysis of

rubbers are included in several technical journals. Perhaps the most complete is the "Summary of Current Literature," published since 1923 by the Research Association of the British Rubber Manufacturers. The French journal, *Revue générale du caoutchouc*, has more recently included a section, Documentation Analytique, covering the same field. The "Annual Report on the Progress of Rubber Technology," published by the Institution of the Rubber Industry since 1937, briefly mentions all articles in connection with rubber. *Chemical Abstracts*, published by the AMERICAN CHEMICAL SOCIETY, and *British Chemical Abstracts* have sections devoted to abstracts of the rubber literature.

Several excellent review articles have appeared in recent years. In 1944 the British Ministry of Supply published a booklet known as "Users' Memorandum No. U.9," which is generally considered the first paper of its kind to give a systematic scheme of analysis of natural and synthetic rubbers. Stern (*199*) and Wyatt (*243*) in the same year wrote review articles which dealt chiefly with methods of identification of natural and synthetic rubbers. In 1945 Wake (*223*), in an excellent critical compilation of the methods used to determine the nature and amounts of rubber present, discussed a recommended analytical scheme in considerable detail for the analysis of vulcanized rubber. Tyler and Higuchi's review (*215*) in 1947 covered the history of the methods of quantitative chemical analysis of synthetic rubber. Both of these latter reviews included much information not previously published.

In 1947 the British Ministry of Supply revised and brought up to date its users' memorandum to give the latest detailed directions for the identification and estimation of natural and synthetic rubbers (*43*). Outlines for the identification and chemical analysis of rubber and rubber products are sometimes included in reference books (*80, 195*), but because books are usually not kept up to date it is suggested that A.S.T.M. methods, Users' Memorandum No. U.9, or similar publications be consulted for the latest methods.

Much of the work on synthetic rubber which was restricted during the war still remains unpublished, but it is hoped that this information will appear in scientific journals during the next year or two. In the early part of the synthetic rubber program in this country the analytical procedures were the same as for natural rubber. Because they were either not suitable or too slow for the rapidly moving synthetic rubber program, new or improved methods were developed. Research sponsored by Rubber Reserve in industrial, university, and government laboratories, on analytical methods and standardization of testing procedures in government synthetic rubber plants increased the precision and accuracy of rubber testing severalfold (*149, 203*). Many of the methods developed for synthetic rubber will undoubtedly also be found useful for the analysis of natural rubber.

More and more the new analytical procedures employ the instruments of the physical chemist and physicist, such as the refractometer, polarograph, electron microscope, mass spectrometer, colorimeter, spectrometer, and x-ray diffraction apparatus. In these procedures the identity of the material is usually not destroyed during test, less sample is required, and results are obtained in a shorter time.

RUBBER IN PLANT TISSUES

Because of the great shortage of natural rubber during the war extensive work was done on methods of identification and analysis of rubber in plant material. The regional laboratories of the U. S. Department of Agriculture studied the possibilities of obtaining rubber from home-grown plants, chiefly the goldenrod, cryptostegia, kok-saghyz, and guayule. By means of staining and microscopical techniques Rollins, Bailey, and deGruy (*180*) were able to demonstrate the location of the rubber in the chlorophyllous cells of the goldenrod leaf. Whittenberger and his co-workers (*229, 231, 232*) studied sections of both fresh and preserved stem and leaf tissues of cryptostegia under a microscope, and were able to identify the rubber by methods of staining, solubility behavior, micromanipulation, x-ray diffraction, and chemical analysis. By micromanipulation they could also stretch the rubber globules as much as tenfold.

Fernández and Núñez (*72, 73*), in determining the rubber content of a great number of rubber-bearing plants growing in Spain, found the old nitrosite precipitation method (*120*) very satisfactory. They also developed a modification (*155*) of the original Stolbin method (*205*) for estimating the amount of rubber in the roots of kok-saghyz. The new method is still empirical, as the amount of rubber is not measured directly. Most of the work on kok-saghyz, however, has been done by the Russians. Filippov (*77*) estimates the amount of rubber in the roots by noting the thickness of the latex film in a transverse section of the root. Another procedure (*152*), which is good only for rough field work, is to place a drop of latex from the live roots in a test tube containing a known amount of water, and then estimate the turbidity. A much more reliable procedure (*196*) disintegrates the plant tissue in an alkaline solution which separates it from the rubber.

Bennett (*29*) determined the composition of rubber obtained from various botanical sources. The percentage of rubber hydrocarbon, the quantity and nature of the acetone extract, and the amount of "insolubles" in nitrobenzene have proved especially useful in characterizing the natural rubbers. *Cryptostegia grandiflora* was studied by Stewart, Bonner, and Hummer (*200*) to determine yield, composition, and other characteristics of its latex. Van der Bie (*31*) published a method for determining the rubber content of Hevea leaves, in which the dried leaves are first extracted with acetone or alcohol, and then extracted with benzene to remove the rubber, which is subsequently refluxed with 0.5 N alcoholic potassium hydroxide.

The classical method of Spence and Caldwell (*197*) for the determination of quantity of rubber in rubber-bearing plants, especially guayule, has been made more rapid by Holmes and Robbins (*99*) and by Willits and co-workers (*235*).

They boil the ground plant tissues in a stronger acid solution for a shorter period of time, heat in an autoclave for a shorter period of time, and then give a shorter acetone extraction previous to the benzene extraction. The newer procedure does not require the addition of an antioxidant to the rubber because of the decreased drying time and a lower drying temperature. Holmes and Robbins seemed to have been worried about the process, in that the rubber extract would include gutta-percha if present in the plant. However, Hendricks, Wildman, and Jones (*96*) have shown by means of x-ray diffraction analyses on rubbers from a large number of plants that nature does not produce both the cis and trans isomers of polyisoprene in the same plant.

Traub (*214*) has developed a rapid photometric semimicro method for determining rubber and resins in guayule tissue. The procedures are adaptable not only to other plants but also to the determination of rubber in uncured crude-rubber products, and may be valuable in the analysis of synthetic rubbers. Solution of the rubber is accomplished by means of oxygenated solvents with relatively high boiling points (115° to 230° C.) which permit solution in 20 to 30 minutes. After the addition of a protective colloid the rubber is precipitated by acidified alcohol, and the degree of turbidity is measured by means of a photometer. The quantity of resins is determined in a similar manner but precipitation is made by acidified water. The author claims an accuracy of about 4% for the method.

LATEX

Relatively little work seems to have been done during the past several years to change or improve the older routine chemical test methods such as total solids, dry rubber content, ammonia content, and pH, on natural-rubber latex (*44, 59, 78, 219*). Ferrand (*74*) developed a micromethod by which it is possible to determine the total solids of latices, using alcohol as a coagulant.

Compagnon and Le Conte (*58*) reduced the time required for the procedure from 24 hours to 2 or 3 hours and modified it so as to give dry rubber content instead of total solids. The method is claimed to have a precision of about 2%. Because of the viscosity of latex, Smith (*193*) states that a hydrometer cannot be used with great precision in the determination of total solids or dry rubber content in undiluted latex. By diluting the latex 1 to 2 the error is decreased, but corrections must be made for variations in temperature of the latex. For an approximation of the dry rubber content of Mangabeira latex it was found (*27*) that when density measurements are used the density–dry rubber content tables used for Hevea latex can be applied.

Brass and Slovin (*42*) developed a "latex strainability test" which measures the amount of latex that passes through a filter medium before clogging. Baker (*18*) and Boucher (*39*) have discussed the stability tests of latex, and state that the high-speed stirring should be performed on latex after an addition of zinc oxide in order to determine ionic stability as well as mechanical stability. Whittenberger and Brice (*230*) developed a rapid method for estimation of the quantity of rubber in guayule latex dispersions. They make use of a microscopic count on one drop of latex. The method requires standardization against a known procedure.

Hessels (*97*) studied the dispersoid analysis of Hevea latex by both the photomicrographic and the sedimentation techniques. The latter method proved to be the most suitable for the separation of the latex into a series of fractions. Altman (*4–6*) developed and described in detail a general scheme for the analysis of the organic constituents of Hevea latex. He isolated and identified various groups of organic compounds such as proteins, lecithins, amino acids, alkaloids, and sterols.

A.S.T.M. Committee D-11 on Rubber and Rubberlike Materials has recently appointed a subcommittee to study test methods for determining the quality of latex. This subcommittee is now revising older methods and will soon offer a set of tentative procedures to the A.S.T.M. The detailed procedures for the chemical testing of GR-S synthetic rubber latices, made public by Rubber Reserve (*156*, *220*), include methods for total solids, residual styrene, soaps, pH, surface tension, turbidity, viscosity, coagulum, and filterability.

Three publications (*100*, *144*, *234*) have described devices for the sampling of synthetic rubber latices during the polymerization reactions that take place under positive gage pressure. Sampling of the mixture while undergoing reaction is necessary in order to study induction periods, rates of polymerization, etc.

EXTRACTS

If rubber is from a "wild" source rather than from a plantation it is probably contaminated with sand, bark, etc. By washing on a mill most of this foreign material is removed, and the percentage loss of weight in this washing process is called "shrinkage" (*26*, *60*). Because the rubber is dried only after and not before the washing, the shrinkage includes original moisture in the sample. Some of the water-soluble constituents of the rubber, including a portion of the natural antioxidants, are also removed from the rubber. The better grades of natural rubber and the synthetic rubbers do not require this shrinkage test.

Acetone extraction has long been the procedure by which most of the organic nonhydrocarbon constituents of natural rubber are removed (*7*, *45*, *216*). The application of this method to synthetic rubber for the removal of fatty acid, etc., in GR-S has not proved to be satisfactory, chiefly because the soap in the rubber tends to polymerize the acetone, and cause erroneous results. It was discovered in 1943 by Baker and Heiss (*79*) that the ethanol-toluene azeotrope (commonly known as E-T-A), which is composed of 70 parts by volume of ethanol and 30 of toluene, is a very good swelling agent for the rubber and a good solvent for the nonrubber organic constituents including soap. This ex-

traction has since become the official procedure of Rubber Reserve (*156*). Instead of using the Soxhlet type of extraction the sample is allowed to reflux directly with the ethanol-toluene azeotrope in the flask, and the time of extraction is thereby decreased from an overnight procedure to one requiring a couple of hours. The per cent of extract is not measured directly but is calculated from the loss in weight of the rubber after removing the solvent. The ethanol-toluene azeotrope extract is used for determining the soap and fatty acid in the rubber (*156*, *203*, *215*).

Kolthoff, Carr, and Carr (*116*) recommended the addition of 10 volumes of water to 100 volumes of the ethanol-toluene azeotrope extraction mixture. They claim that the addition of water to the mixture has no deleterious effects on the rate of extraction, and has the advantage of preventing the solution of the low molecular weight polymer. Both the azeotrope and acetone dissolve these low polymers which occur in synthetic rubber to the extent of 1 to 3% but are practically nonexistent in natural rubber. The official procedure of Rubber Reserve (*156*), however, requires the use of anhydrous ethanol-toluene azeotrope except for alum-coagulated GR-S rubber for which the azeotrope containing 5% of water is used to hydrolyze the aluminum soaps and permit the fatty acids to be extracted.

A method often used for extracting the rubber hydrocarbon from an unvulcanized acetone-extracted sample of rubber by chloroform or benzene is not always quantitative if run the usual short period of time. In some cases the extraction must continue for 100 hours or more before the rubber hydrocarbon is completely extracted (*69*).

The general methods for extractions by chloroform, acetone-chloroform mixture, and alcoholic potassium hydroxide have undergone no significant changes the past few years. Several notes, however, have described improvements in extraction apparatus. Boyd (*40*) uses a crucible holder in the rubber apparatus which eliminates the necessity of attaching the sintered-glass crucibles to the condensers by means of wires. He also (*41*) has a scheme for the recovery of chloroform by means of a take-off from the rubber extraction apparatus. Messenger (*148*) suggests a modification in the all-glass extraction apparatus often used in England. In the modified form it can be connected to a condenser after extraction and the solvent distilled off. Kemp and Straitiff (*112*) have designed a drying apparatus which involves a high temperature and a moving inert gas at low pressures. It is used for the efficient removal of water, acetone, benzene, etc., from unstable polymeric materials.

In determining the "insolubles" in an organic solvent such as toluene (*26*) it has never been understood definitely whether the proteins remain with the insoluble portion or become dissolved along with the rubber in the solvent. Nitrogen determinations on both soluble and insoluble portions (*170*) showed that some of the proteins were distributed in each of these fractions, but that about 80 to 90% of them were present in the soluble portion. This finding will be a surprise to many chemists, who have been under the impression that most or all proteins are insoluble in toluene or benzene.

Solvents for vulcanized rubber often become useful in analysis, especially when certain fillers are present which decompose easily on heating, in which case the organic material cannot be burned from the fillers. The extraction of the vulcanized rubber is discussed in later sections where this dissolution process will be applied.

NATURAL-RUBBER HYDROCARBON

Until recently the rubber hydrocarbon content of natural rubber has been found by difference, by subtracting the sum of the nonhydrocarbon constituents from 100% (*7*, *45*, *216*, *242*) because there was no reliable method for determining the hydrocarbon by direct means. The method, while none too good for natural rubber, becomes more complicated with synthetic rubbers

and their mixtures. Neither is the method very satisfactory when applied to non-Hevea rubbers whose compositions are often low in rubber hydrocarbon content and high in nonrubber constituents.

Natural rubber hydrocarbon can be estimated from the amount of unsaturation in a sample of natural rubber determined by means of the well-known Kemp-Wijs procedure (110). Bloomfield (34) was able to make bromine react additively with rubber, but he found that a correction must be applied when the rubber is in the vulcanized state (35). More is said below about similar procedures in the discussion of methods for the quantitative analysis of mixtures of natural and synthetic rubbers.

Willits, Swain, and Ogg (236) improved an old gravimetric method for the determination of rubber hydrocarbon by precipitating it as an alcohol-insoluble bromide. The method was developed chiefly for the quantitative determination of rubber in extracts of plant material such as guayule, cryptostegia, etc., but was also found to work very well with crude rubber and latices. It cannot, of course, be applied to rubber in the vulcanized form nor to natural rubber in the presence of synthetics.

In 1937 a note in a Russian journal (113) mentioned a new direct method for determining rubber hydrocarbon content. It is based on the method of Kuhn and L'Orsa (121) which involves oxidation of the side-chain methyl groups in organic compounds containing the structure —CH₂—C(CH₃)=CH— to acetic acid, which is then titrated with standard alkali. As application of the procedure to rubber lacked detail, Burger, Donaldson, and Baty undertook to improve the procedure, and worked out conditions for the oxidation of the rubber by means of chromic acid, the separation of the resulting acetic acid by distillation, the aeration of the distillate to remove carbon dioxide, and the titration of the acetic acid (7, 43, 51). This method has considerable advantage over the previously mentioned ones in that it can be used to determine natural rubber in the presence of synthetics. It can also be used for vulcanized rubber, although large percentages of combined sulfur require a correction. Wake (43, 223) gives a curve which shows the correction for all percentages of combined sulfur. Gutta-percha and balata react exactly as rubber hydrocarbon in this method of analysis. Small corrections of known magnitude are to be made when most synthetic rubbers are present.

When no interfering substances are present in the rubber a precision of 1 to 2% is claimed for the procedure. Wake (223) estimates that the standard deviation is about 2%. Results obtained at the National Bureau of Standards (69) indicate that the procedure can give better precision than this. In routine analysis on 59 samples of wild rubber conducted during the war, when speed was essential, the standard deviation was found to be 0.64% rubber hydrocarbon, but at a later date when care was exercised in the same procedure for research work the standard deviation was reduced to 0.16%. Summations of rubber hydrocarbon content, acetone extract, and toluene insolubles were very close to 100%, which indicates good reliability for the method. Pucci and Maffei (169) also found the method very satisfactory. Poulton (163) developed the method of Burger, Donaldson, and Baty into a microprocedure and compared the two methods point by point. Using a 10-mg. sample, he was able to obtain a satisfactory determination of the rubber hydrocarbon in 4 hours, including the time for acetone extraction.

Stewart and Hummer have found that there is an inverse correlation between the quantity of rubber hydrocarbon and an insoluble crystalline fraction in the total solids of the latices of *Cryptostegia grandiflora* (201) and *Hevea brasiliensis* (202).

ELEMENTAL ANALYSIS

In the determination of the constitution and structure of a molecule and also for identification of a compound or mixture, a total quantitative analysis of all the elements present often gives valuable information. Smith, Saylor, and Wing analyzed puri-

fied natural-rubber hydrocarbon (194, 237) and found that the sum of the carbon and hydrogen totals very close to 100%; this indicates the presence of very little, if any, combined oxygen. It is unfortunate that at that time there was no reliable method for an accurate direct determination of oxygen. Since that time there have been developed two good methods based on work by Unterzaucher (217), but no analyses for oxygen have been made on highly purified natural rubber.

The method of Walton, McCulloch, and Smith (226) pyrolyzes the sample in an atmosphere of helium, converts all oxygen to carbon monoxide by passing the pyrolyzed gases over pellets of carbon at 1120° C., and determines the amount of monoxide by an extremely sensitive colorimetric method (189). As little as 0.01% of oxygen can readily be determined by this method. Chambers (55) in a somewhat similar procedure converts all oxygen to carbon monoxide but then oxidizes it to the dioxide by means of iodine pentoxide, and determines the resulting iodine volumetrically with thiosulfate. The method is claimed to be reliable to 1 part in 50 for oxygen percentages below 2%.

Wagman and Rossini (222) describe an extremely precise method for the macroanalysis of carbon and hydrogen. Madorsky (137) used this procedure successfully in the analysis of some butadiene-styrene polymers in order to determine the amount of bound styrene.

Farmer, Tristram, and Bolland (70) studied in detail the Kjeldahl method for the determination of nitrogen. Using a combination of the macro and micromethods, as little as 0.05 mg. of nitrogen has been estimated with considerable accuracy and much less can be detected. They recommended the use of mixed catalysts of sodium sulfate, copper sulfate, and sodium selenate. Cole and Parks (57) developed a semimicro-Kjeldahl procedure for nitrogen determination in the control laboratory, where more speed is required. The method does not determine nitrogen in N—N or N—O linkages, but is especially suitable for nitrile rubbers. Samples of 15 to 50 mg. are used. The catalyst recommended is a mixture of sodium sulfate, selenium, and mercuric oxide. The standard procedures (7, 44, 216) could well be simplified by distilling the ammonia into boric acid solution and titrating the distillate with standard acid (119), using a mixed indicator of bromocresol green and methyl red.

In determining the amount of chlorine in synthetic rubbers Hofmeier and Schroeder (98) tried to develop a method simpler than the classical Carius method. In this procedure the material is oxidized by a mixture of concentrated sulfuric and nitric acids, and the resulting gases are passed through a silver nitrate solution in which the precipitated silver chloride is determined gravimetrically. Stoeckhert (204) describes and criticizes the earlier methods of chlorine analysis and then suggests a new procedure, which dissolves the chlorine of the polymer by means of a fusion with anhydrous sodium carbonate and sodium peroxide. The chloride is then determined by any standard procedure. Phillips (162) uses a combustion micromethod for determining the quantity of chlorine in polymeric materials. The A.S.T.M. (8) recommends combustion in a furnace at about 1300° C. with subsequent determination of the silver chloride by some convenient method. As an alternative procedure it suggests the Parr oxygen bomb method if the sample can be finely divided. No objections seem to be raised to the Carius method for determining chlorine except the great likelihood of explosions. Gordon (85, 86), however, has modified the form and use of the Carius tubes in such a way as to minimize or prevent these explosions.

SULFUR

The relatively large amount of work that is done each year in search for new and better methods for the determination of total sulfur is an indication that the old methods are not entirely satisfactory. There seems, however, to be less controversy with procedures for free sulfur. In spite of a few methods for estimating free sulfur, like the more rapid one of Bolotnikov and

Gurova (*38, 157*) which involves iodometric titration, and the one of Rogov (*179*) in which the free sulfur is oxidized to sulfate by means of permanganate, the standard procedures (*7, 45, 216*) seem to prefer the barium sulfate gravimetric procedure after oxidation of the sulfur by means of nitric acid or by bromine or by a combination of the two. Morley and Scott (*151*) compared the bromine and nitric acid methods of determining the amount of sulfur in the acetone extract and concluded that neither method is entirely satisfactory, but the bromine method is recommended as the better because of its simplicity and rapidity. They used the Carius procedure as a check method. Proske (*167*) determined the free sulfur in a vulcanizate by means of polarographic analysis after extracting the sample with pyridine. The method works well with simple systems but some accelerators were found to interfere.

There is confusion in the use of the term "total sulfur." Some times it includes all the sulfur in a compound and at other times it does not include the sulfur present as barytes or other fillers. Most of the methods for "total sulfur" involve the use of powerful oxidizing agents and therefore may be dangerous because of possible explosion. The standard procedures (*7, 45, 216*) prefer oxidation by nitric acid, bromine, and chlorate, followed by the gravimetric barium sulfate precipitation procedure. Recchia and Carraroli (*172*) oxidize the sulfur in a potassium hydroxide–potassium nitrate fusion mixture, precipitate the sulfate as benzidine sulfate, and titrate it with standard sodium hydroxide. Good results were claimed.

Taranenko (*206*) reports that the method of combustion of the sample in a stream of oxygen gives erroneous results in the presence of zinc, magnesium, and calcium because of the formation of their sulfates. He has overcome this error by using air in place of oxygen, which prevents the oxidation to the sulfate. The combustion gases are passed through absorbers containing silver nitrate, and the liberated nitric acid is titrated with standard sodium hydroxide.

It is understood that the revision of British standard methods (*45*) will include the combustion method for total sulfur. The sample is burned in oxygen at a temperature between 1350° and and 1400° C., at which temperature all the sulfur, including that present as sulfates, is converted to sulfur dioxide.

Jones (*105*) has developed a semimicroprocedure for the determination of sulfur. He oxidizes the sulfur by the perchloric acid method (*240*), but instead of determining the sulfate by gravimetric means he titrates it with barium chloride in the presence of a tetrahydroxyquinone indicator. Luke (*132*) also developed a volumetric microprocedure for the determination of total sulfur in rubber.

The sulfate is reduced to sulfide by means of hydriodic acid. The hydrogen sulfide is distilled off and titrated iodometrically. The method works equally well with perchloric acid or the A.S.T.M. methods of oxidation. The chief disadvantage is that inaccurate results are obtained for samples containing more than 5 mg. of sulfur. Later Luke (*133*) modified his procedure so that correct results are obtained for samples containing up to 100 mg. of sulfur. The sulfide in this procedure is distilled at a lower temperature, absorbed by ammoniacal cadmium chloride, and oxidized with an excess of standard potassium iodate solution. The excess iodate is titrated with sodium thiosulfate solution.

Cheney (*56*) proposes a modification of the A.S.T.M. oxidation procedure. After the nitric acid–bromine oxidation more nitric acid is added, and to the boiling solution small portions of potassium chlorate are added. In hundreds of analyses no explosions occurred when the solution was kept boiling. He checked his analyses by the Parr bomb method.

Hammond and Morley (*90*) compared the perchloric acid, the Carius, and the sodium peroxide–sodium carbonate fusion methods for oxidation of sulfur in rubber compounds. They found that the Carius method gave results closest to theory, the perchloric method gave somewhat low results, especially with ebonite,

and the fusion method gave good results for ebonite but high values for soft rubbers. They discuss the dangers of the explosive tendencies of the perchloric and the fusion methods. They also suggest an upper limit of 500° to 600° C. for the ignition of the barium sulfate because of decomposition at higher temperatures.

Rehner and Holowchak (*175*) determined the amount of total and combined sulfur in Butyl rubber. Procedures used for natural rubber are not applicable because Butyl rubber is less permeable to acetone and more stable to oxidizing agents. For the determination of free sulfur the authors recommend an extraction by methyl ethyl ketone instead of acetone. For total sulfur the sample is burned in the Braun-Shell sulfur apparatus.

Of the methods used in oxidizing the sulfur to sulfate, the perchloric acid procedure seems the least popular because of its explosiveness. It is, however, preferred by Luke (*132*) to the A.S.T.M. method when materials difficult to oxidize are present. The fusion method is rather time-consuming. The Parr bomb method (*13*) is safe and yields excellent results but the sample must be very finely divided by rasping, buffing, or grinding. Cheney (*56*) says that with thioplasts stable sulfones are produced in usual oxidation procedures, so that the instantaneous oxidation by means of a bomb is necessary. The Carius method is probably the best standard method at present, but is not popular because of the breakages of tubes during oxidation. Gordon (*85, 86*) has studied the Carius procedure and has greatly reduced these losses by using a better method for sealing and protecting the tubes.

Sheppard and Sutherland (*190, 191*) made some infrared studies on the vulcanization of rubber. The intensity of a band at 960 cm.$^{-1}$ correlates well with the amount of sulfur chemically incorporated with the rubber but not at all with the degree of vulcanization as indicated by the physical properties of the vulcanizate.

TRACE ELEMENTS

Many elements exist in both natural and synthetic rubbers. Copper and manganese are often determined because their presence accelerates the deterioration of natural rubber. The Vanderbilt handbook (*15*) describes qualitative tests for determining the presence of these two metals. In quantitative analysis of vulcanizates the wet oxidation of the organic material seems to be preferable in standard procedures (*7, 45*) to the ignition method. It is believed there is less chance for loss of material. The British standard methods for determining the copper or manganese in crude or unvulcanized compounded rubber (*44*), however, employ a preliminary ashing procedure. It is known that a great many laboratories in their own procedures also ash the samples first because of the greater simplicity of sample preparation. Vila (*219*) recommends ignition at a low temperature, 400° C.

Instead of the usual procedure of measuring the color of an aqueous solution of sodium diethyldithiocarbamate, the solution is extracted with carbon tetrachloride and then the color intensity of the extracted solution is determined either by means of Nessler tubes or a colorimeter. Cassagne (*54*) states that diethyldithiocarbamate gives color reactions with iron, manganese, and zinc, and that these disturbing elements must be removed. After rendering the silica insoluble, disodium phosphate is added in an ammoniacal medium to separate the previously mentioned metals. After filtering, either ether or isoamyl alcohol is used to extract the copper color, which is then measured in any of the usual ways. In order to free the copper from disturbing elements van der Bie (*33*) first separates the copper from the ash solution either by microelectrolysis or by precipitation as a sulfide. The copper is then determined colorimetrically by the diethyldithiocarbamate method.

The polarograph (*207*) has been used successfully in a very simple procedure for determining the amount of copper in rubber.

The ash of the rubber is dissolved in 1 to 1 hydrochloric acid, the solution is evaporated to dryness, and the residue is dissolved in 5 ml. of supporting electrolyte composed of 1 M ammonium hydroxide, 1 M ammonium chloride, and 0.02% gelatin. The polarographic measurements require but a few minutes for completion.

In the determination of manganese Vila (219) deviates from the standard procedures in that he recommends ashing in a muffle furnace and a subsequent fusion with potassium bisulfate. The usual oxidation to permanganate by means of periodate is made, followed by the colorimetric comparisons.

The determination of iron has recently become more important because of the greater effect of iron than of copper or manganese on the aging of GR-S (2). Van der Bie (30) developed a procedure for quantitatively determining small amounts of iron in rubber by a color reaction with ammonium thiocyanate. Because of the great volatility of ferric chloride, sulfuric acid should be added to the rubber in the crucible before ignition can be made at 500° C.

McGavack (135) measured the quantities of copper, manganese, and iron in ashed samples of a number of different rubbers by means of a grating spectrograph.

Van der Bie (32) was able to determine minute quantities of phosphate, calcium, and magnesium in rubber.

From a solution of the ash the phosphate was determined colorimetrically by the blue colloidal phosphorus-molybdenum complex which is obtained by reduction with stannous chloride. Calcium from another ashed sample is precipitated as oxalate and then determined oxidimetrically. Magnesium is precipitated as magnesium ammonium phosphate and then the phosphate determined as previously described. In order to prevent losses of the elements in question, special ashing procedures must be followed.

Kelley, Hunter, and Sterges (108) describe methods for the determination of small quantities of nitrogen, phosphorus, potassium, calcium, and magnesium in tissues of rubber-producing plants. Barnes and his co-workers (25) found that a method involving ultraviolet spectrochemical analysis worked well in determining quantitatively 23 different trace elements in rubber compounds.

IDENTIFICATION OF RUBBERS

The introduction of the various types of synthetic rubbers and the use of mixtures of them in compounding have made the problem of identification a very important one. The identification of natural rubber in plant tissues is discussed above.

Some rubbers may have such well-defined general characteristics as odor, freeze resistance, etc., which may render unnecessary any further tests for identification.

Determination of density of a sample, especially of the raw material, often gives a very good indication of its identity. Precision of almost 1 part in 10,000 can be obtained if hydrostatic weighings are made on rubber samples that have been freed from gas bubbles (241). For less precise work Feldman (71) makes use of a set of solutions of densities in increments of 0.03 from 1.00 to 1.93. By watching the floating tendencies of samples their densities can be estimated to the nearest second decimal. Users' Memorandum No. U.9A (43) gives a table of the densities along with the chemical composition of over 50 different synthetic rubbers.

One of the oldest of all chemical tests for natural rubber, the Weber color test (227) developed in 1900, has finally become very valuable. It has been studied by Stern (43, 199) who modified the test somewhat and also applied it to the synthetics. Parker and Wake (8, 161) found the test to be distinctive for the grouping —CH₂—C(CH₃)=C< occurring in linear polymers. The acetone-extracted rubber is brominated in carbon tetrachloride solution, phenol is added, and heating then develops a violet color. A strong positive reaction is also obtained from synthetic polyisoprene, methyl rubber, Neoprene FR, gutta-percha, and

balata. Faint violet color is obtained from Butyl rubber and from Pliofilm. A trichloroacetic acid color test described by Wake (223) is a good check on the Weber test. Fusion of the rubber with the acid gives a yellow-red color, heating the fused mixture to boiling darkens the color to orange-red, and dissolving the mixture in water gives a violet-gray precipitate.

Much information on an unknown synthetic rubber sample can be obtained from qualitative tests for sulfur, chlorine, and nitrogen. Stern (199) describes a test whereby all of them can be determined on one sample treated with metallic sodium. Addition of silver nitrate to one portion of this mixture will indicate whether or not chlorine is present. Sodium nitroprusside added to a second portion gives a violet color if sulfur is present. Adding ferrous sulfate and ferric chloride, and boiling with hydrochloric acid gives a deep blue coloration if nitrogen is present. A chlorine-containing polymer gives a characteristic color if the rubber is placed in a flame (171), but confusion may result from the presence of chlorine-containing softeners. Beilstein's hot wire test (49, 153) is equally as simple and characteristic for chlorine. Roberts (176) proposes a stain test for chlorine compounds in which he volatilizes the sample and passes the vapors past filter paper soaked in chromate or dichromate. A bleaching of the color indicates the presence of chlorine.

In 1944 Burchfield published a paper (48) on the identification of natural and synthetic rubbers which was based on the pH and the specific gravity of the pyrolysis products of the rubber. The tests can be performed in a few minutes and give at least a classification of the sample into one of several groups. Confirmatory tests are then required to determine the particular rubbers. A few drops of the distillate are added to each of two solutions. Tables describe the colors produced by the different rubbers and also tell whether distillates float or sink in the solutions. The following year Burchfield (8, 49) rearranged the procedures of his previous pyrolysis tests and added new ones to include more synthetics. He also described spot tests in which filter papers impregnated with various solutions are held over the smoke emitted from a sample of rubber heated by means of a red-hot metal rod. These spot tests are more rapid and convenient but are not so conclusive as the laboratory pyrolysis tests. The author suggests a possible quantitative procedure by analyzing pyrolyzates prepared under very carefully controlled conditions. Users' Memorandum No. U.9A (43) describes many identification tests used for the various types of synthetic rubbers.

Parker (159) studied the "reaction time" of acetone-extracted rubberlike polymers in a mixture of concentrated nitric and sulfuric acids. The time is noted for the start of disintegration of the rubber. This simple test seems to be sufficient for the nitrile, styrene, and isobutene types, but polychloroprenes, thioplasts, and natural rubber require additional data. From this reaction time it is also possible to determine roughly the ratio of two known rubbers in a mixture.

Powers and Billmeyer (164) discovered that the logarithm of the percentage swelling varies inversely with the aniline point up to 100% swelling, and therefore believe that the slope of the swelling curve is a fairly satisfactory index for identification of the type of synthetic rubber. About the same time Parker (160) published an article on the identification of raw and vulcanized rubberlike polymers by determining their swelling ratios at 25° C. in benzene, light petroleum, and aniline. He found that the ratios of swelling for the different types were different and independent of the state of vulcanization and the nature and amount of fillers present in the mixture. This experiment gives six possible swelling ratios. If the logarithm of one ratio is plotted against the logarithm of a second ratio, each type of rubber occupies a definite spot or area on the graph. The swelling ratios of unknown samples of rubber are compared with the data obtained from known rubbers. The method is sound in principle and very useful in practice but requires about a week's time for completion.

Parker (158) found that the determination of sulfur by the method of Bolotnikov and Gurova (38) can be used successfully to differentiate the tetrasulfide Thiokols, A and AZ, from the disulfide Thiokols, F and FA. The disulfides contain about 50% of sulfur and the tetrasulfides about 80%. Determining the composition of mixtures of the two is very difficult, but amounts may be estimated by analyzing for the sulfur content existing in the various forms (43).

Only very recently has the mass spectrometer become an analytical tool. Madorsky and Straus (140), by a high-vacuum pyrolytic fractionation of polystyrene, were able to analyze some of the fractions by means of the mass spectrometer, thus developing a technique for the polymer's identification. Wall (225) also applied the mass spectrometer to the thermal decomposition products of other polymers. He found that under his conditions of pyrolysis the polymers produced chiefly the monomers from which they were produced. Madorsky (139) separated the pyrolysis products of several polymers into three fractions: gaseous, liquid, and waxlike solid. Mass spectrographic analysis of the liquid fraction gives a spectrum that is characteristic of a given polymer.

Barnes and co-workers (25) have found it possible to distinguish between natural and synthetic rubbers by determining the quantity of phosphorus present. Natural rubber contains usually from 300 to 500 parts per million whereas the synthetics usually contain less than 50. This method is, however, likely to result in false conclusions, for some of the recent synthetics now contain an organic phosphorus-containing age resistor.

Gehman (83) has published an article on the use of x-ray diffraction methods in rubber testing. Resins, plastics, and different types of rubber can be identified by this procedure. Crystallinity can also be identified by use of this technique.

From the form, color, and odor of a raw rubber, its nitrogen content, and its swelling property, Kluckow (114) was able to identify natural rubber and the German synthetic rubbers such as Buna S, Buna SS, Buna 85, Perbunan, Perbunan Extra, Buna SSGF, Buna SSE, Buna SR, and Buna SW. Marek (143) distinguished between the various German Buna rubbers and natural rubber by measuring the refractive indexes of their distillates. By bromine addition (142) he was also able to differentiate the different types of smoked natural rubbers. He found a relationship between bromine numbers and the plasticity of a rubber. By means of a dye-staining technique DeGruy and Rollins (62) were able to detect the extent of penetration of latex in tire cords.

Shaw (187) in 1944 published a schematic procedure for the identification of synthetic resins and plastics, in which rubbers are included. A section on identifications in "Modern Plastics Encyclopedia" (150) also contains procedures for rubber. The latter contains tables on burning characteristics, solubilities in organic liquids, color identification tests, and microscopic staining tests. Wake's summary article (223) contains considerable detail and critical analysis of the methods of identification used up to 1945. Probably the most complete article on the subject published at the present time is the Ministry of Supply's 1947 edition of the users' memorandum (43). It contains a summary of the characteristics of the main types of rubbers and also a scheme for the systematic qualitative analysis of mixtures.

For the identification of polymers in mixtures other techniques have been introduced, such as infrared spectroscopy, ultraviolet spectroscopy, and chromatographic analysis, but as these methods have also become useful in quantitative estimation they are discussed in the following section. The identification of fillers and compounding ingredients is dealt with in still another section.

QUANTITATIVE ANALYSIS OF RUBBERS

The amount of rubber in a sample is often determined by the "difference" method. The estimation of natural rubber can be made by a direct method, but such procedures are not yet available for many of the synthetic rubbers, especially if present in mixtures with other types. If natural rubber and some synthetic rubber such as GR-S are present in a compound the total rubber can be determined by the "difference" method and the natural rubber by the direct chromic acid oxidation procedure (51), thus defining the quantity of GR-S. Le Beau (126) used this method for determining the relative quantities of natural rubber and GR-S in reclaimed rubber. The results obtained from the chromic acid oxidation method required the application of a correction which is dependent on the type of reclaim in the mixture. Newton (153), however, believes the uncorrected values obtained for natural-rubber hydrocarbon in reclaim to be closer to the "true" values or the amount of rubber which is available for vulcanization.

Kemp and Peters (111) applied the method of iodine chloride addition to the determination of unsaturation in butadiene and related polymers. Hot p-dichlorobenzene was used to dissolve the rubber mixture. By measuring the unsaturation of styrene or nitrile rubbers the percentage of butadiene in the polymers can be calculated. Wake states that inefficient dissolution of the rubber is the most probable source of error in Kemp and Peters' method and he therefore modifies it somewhat (43, 223). Kobeko and Moskvina (115) also used the iodine chloride method for determining the unsaturation in butadiene synthetic rubbers but found that solution of the rubber was facilitated (less tendency to precipitate) with dichloroethane. Vasil'ev (218) used a similar procedure but added iodine bromide to the rubber rather than iodine chloride. Lee, Kolthoff, and Mairs (129) made an extensive study on the addition of various chemicals to the double bonds of natural and synthetic rubbers and found that iodine chloride was the most suitable addition agent. They modified the method of Kemp and Peters (111), and thereby produced a precise method for use with polybutadiene, polyisoprene, and their copolymers with styrene (129). From their "exact" but elaborate procedure they formulated a simpler method to be used for each type of polymer and copolymer.

Unsaturation in synthetic rubbers includes internal double bonds (in the main chain), which are caused by 1,4 polymerization, and external double bonds (in the side chains), which are caused by 1,2 and 3,4 additions. Yakubchik, Vasil'ev, and Zhabina (244) developed a rapid method for determining the characteristic chemical structure of the butadiene polymers (internal and external double bonds) which is based on the amount of formic acid and formaldehyde formed in the decomposition products of their ozonides. Kolthoff and Lee (117) and Saffer and Johnson (181) developed procedures for the determination of the external and internal double bonds in synthetic rubbers which depend on the differences in reaction rates of perbenzoic acid with these two types of double bonds.

The previously mentioned procedures cannot be applied to determine the unsaturation in Butyl rubber. The development of a method for this rubber was necessary because the rate of cure of the polymer and the properties of the finished product are dependent on the amount of unsaturation in the raw rubber. Rehner (173) studied the additions of several chemicals, including iodine chloride, to the double bonds of Butyl rubbers. He found the most reliable method to be one based on the limiting viscosity of the polymer after degradation by ozone. The method assumes that the polymer chain is broken at the double bonds and that the limiting viscosity is a measure of the mean size of polymer fragments existing originally between the successive double bonds. Rehner and Gray (174) correlated values obtained from this method of ozonolysis with those from addition of iodine chloride. The latter method was used with the aim of facilitating routine work.

Gallo, Wiese, and Nelson (81) developed a good addition method for Butyl rubbers which adds iodine in the presence of mercuric acetate and trichloroacetic acid. The excess iodine, as

in previous procedures, is titrated with standard thiosulfate. The method is recommended only for polymers where the unsaturation is derived from isoprene. The total time required for the determination is 1.5 hours as compared with 24 hours for the less precise iodine chloride method. This shorter method is to be preferred for routine analysis over the more complicated ozone-degradation procedure.

Chemical spectroscopy has in recent years become a valuable tool in the structural diagnosis of large molecules. In this way it is possible to identify the presence of particular molecules and to estimate the amount of each. Earlier work was chiefly concerned with ultraviolet spectra but the infrared technique soon swept ahead in the analysis of synthetic rubbers. Barnes and co-workers (23, 25) determined the infrared spectra for natural rubber and several of the synthetics with which the spectra of unknown samples could be compared. For quantitative estimations light transmission is measured at a particular wave length. Several good articles have described the theory of infrared spectroscopy, the background necessary for its use, and its applications (21–25, 102, 190, 191, 208, 209, 212, 213). Thompson (208) and Field, Woodford, and Gehman (76) have shown the value of infrared spectroscopy to the study and analysis of 1,2 and 1,4 additions of conjugated dienes. The proportions of each type of unsaturation are quickly revealed. Thompson and Torkington (210, 211) have determined the infrared spectra for natural rubbers, synthetic rubbers, other high polymers, and their monomers.

Dinsmore and Smith (65) presented an extensive study of the applicability and limitations of infrared methods for the identification and quantitative analysis of the rubber content of commercial articles of natural rubber and some of the common synthetics. They give detailed procedures for the preparation of the rubber films for the spectrometer, for the analysis of GR-S blends, and for the determination of nitrile content. They claim an accuracy of about 1%. The spectra of vulcanized compounds are not significantly different from those of the unvulcanized rubbers. Saunders and Smith (183) determined the infrared spectra of natural rubber from a number of different sources such as Hevea, guayule, and kok-saghyz, and found them to be nearly identical after they had been extracted by acetone. The infrared method was useful in determining the nature of the impurities of the rubber and thus may be used in identifying the source of a natural rubber. The authors found the infrared spectra of purified gutta-percha, balata, and chicle similar to each other but different from those of the natural rubbers, undoubtedly because of the trans configuration of the former and the cis of the latter substances.

Le Beau (127) used the infrared technique to show that oxygen does not enter the hydrocarbon chain as C—O or as O—H during the reclaiming processes in natural rubber.

Landler (125) fractionated GR-S, Perbunan, and Vistanex by chromatographic separation. A filtered solution of the mixture in toluene containing some methyl alcohol was passed through a column of carbon. The various layers were separated mechanically and the separated polymers dissolved in good solvents. The work was only of preliminary nature but showed that preferential absorption is practicable as a procedure in separating different polymers.

Parker (158) showed that it is possible to extract polyisobutylene from vulcanized rubber by the use of petroleum ether. The sample is previously extracted with acetone. The method is simple and is free from interference by carbon black. It is much more reliable, especially at higher concentrations of polyisobutylene, than the A.S.T.M. nitric acid method (8). For the determination of GR-I, which is insoluble in petroleum ether when in the vulcanized state, the molecules can first be split by means of nitric acid, leaving polyisobutylene which can then be extracted with petroleum ether (43).

An important chemical control in the production of GR-S synthetic rubber is the determination of the content of combined styrene. By precise determination of carbon and hydrogen the percentage of bound styrene can be computed, but this method is too lengthy and complicated for routine check (111, 137). The iodine chloride addition method (111) was not found useful because of side reactions (215). Baker and Heiss (19, 79) in 1943 turned their attention to a method of refraction based on interferometer measurements of rubber solutions, after abandoning the use of ultraviolet absorption because it is highly sensitive to impurities. Meehan (145) investigated the ultraviolet absorption method in much greater detail, and concluded that the probable relative accuracy of the method can be made to be about 3%. Madorsky and Wood (133) developed a procedure based on refractive index measurements on GR-S following the work of McPherson and Cummings on natural rubber (136). The relation of index to the percentage of bound styrene (215) was then derived by Madorsky and Wood from measurements on a series of samples for which the bound styrene content had been determined from the carbon-hydrogen ratio (137). This refractive index procedure has been used since 1945 in inspection testing in the GR-S plants (149, 203). Wiley and Hobson (233) have also studied the techniques for measurement of refractive index and describe preferred procedures for specific polymer types.

Meehan, Parks, and Laitinen (146) compared the methods of ultraviolet absorption and chlorine analysis applied to the determination of the composition of butadiene-chlorostyrene polymers and found them to be in good agreement. The percentage of chlorine was determined by amperometric titration of the chloride ion after a sodium fusion of the polymer. The accuracy of the spectrophotometric method is about 3 to 4%. Laitinen, Miller, and Parks (123) also studied the ultraviolet absorption of vinyl polymers and their monomers and developed a method which can be applied successfully to the determination of monomer ratio in copolymers of butadiene and substituted vinyl aromatic compounds.

An oxidative degradation method recommended by the A.S. T.M. (8, 215) produces p-nitrobenzoic acid from the styrene links. This acid is titrated by means of standard alkali. The results obtained are not very accurate, especially with high-styrene rubbers. The method was recommended in the 1944 users' memorandum, but was omitted from the 1947 edition (43) because it was found less accurate than originally thought.

FILLERS

There is no definite procedure by which fillers in a vulcanizate can be measured. Sometimes they can be determined by means of ashing; at other times they must be separated from the rubber by methods of solvent extraction. One section of the Vanderbilt rubber handbook (16) is devoted to the identification of rubber chemicals, which includes tests for various types of mineral fillers. Scott (185) studied the changes that occur in some mineral constituents of rubber during incineration. He concluded that whiting will lose carbon dioxide unless the temperature is kept below 500° C. Addition of ammonium carbonate to the sample, however, keeps the crucible rich in carbon dioxide and thus minimizes the loss. Litharge promotes the decomposition of whiting, forming calcium metaplumbate. If whiting and chromic oxide are both present, calcium chromate may be formed on ignition.

Many solvents have been used for the extraction of rubber from the fillers. The A.S.T.M. (7) uses a mineral-seal oil which dissolves the rubber in about 2 hours at 130° to 150° C. Hublin (101) studied the use of other solvents—e.g., naphthalene, α-nitronaphthalene, nitrobenzene, anisol, and o-nitroanisol. Of these he found the o-nitroanisol the best, dissolving the rubber in from 20 to 60 minutes at 100° to 120° C. The author claims greater precision than is obtainable from the A.S.T.M. method. Barnes and co-workers (25) in 1944 said that the then currently

used solvents for extracting rubber from the fillers did not give sufficiently good separation for a subsequent infrared spectroscopic examination. They also tried a number of solvents and found the best for their purposes was p-cymene mixed with a small amount of xylene. This gave a clear solution of rubber even when carbon was present in the sample. Dinsmore and Smith (65) found that o-dichlorobenzene dissolves all types of vulcanized rubbers.

Wake (224) studied the rates of dissolution of natural rubber, GR-S, and Butyl rubbers in p-dichlorobenzene, nitrobenzene, p-cymene, Decalin, and α-nitronaphthalene. His data show the process is essentially oxidative, and he recommends bubbling air through the mixture during the dissolution of the rubber, especially at the early stages, to speed up the reaction.

The methods already described for extracting vulcanized rubbers from the fillers are not suitable for use with the neoprenes or with Butyl rubber because of their difficulty in dissolving in the solvents mentioned above. Scott and Willott (186) devised a method applicable to the polychloroprenes but it does not work satisfactorily with the nitrile rubbers. The rubber is swelled in nitrobenzene before nitric acid is added. Xylene is later added and the fillers are filtered off. McCready and Thompson (134) determine the free carbon in Butyl compounds and reclaim by a modified A.S.T.M. procedure which omits the acetone-chloroform extraction but adds a digestion in mineral-seal oil before the nitric acid treatment. Galloway and Wake (82) quantitatively separate the polymer from the fillers in vulcanized Butyl rubber by extracting it with light petroleum after a nitric acid treatment. They also omit the previous acetone extraction.

The A.S.T.M. method (7) for the determination of carbon black, which involves the decomposition of the rubber by hot nitric acid, employs an empirical correction because of the high results it gives. The hazardous nitric acid procedure contains a slow filtering process and also gives high results. This led Roberts (177) to recommend the digestion of the rubber in hot cresol and then the separation by filtration of the fillers, including the carbon black. The soluble material is removed by washing, the volatile substances are driven off by heating in an atmosphere of carbon dioxide, and the carbon is then burned in air. The wet oxidation method is gradually being replaced by pyrolytic methods for removing rubber from fillers.

Dekker (63) pyrolyzes the acetone-extracted rubber at 425° to 450° C. in a stream of nitrogen gas. The residue is then treated with acid, filtered, dried at 150° C., and weighed, and the carbon is determined by ashing. The official method for determining carbon black in GR-S Black (156, 215) employs a pyrolysis at 550° C. for removing the rubber before burning the carbon. Werkenthin (228) describes the Bureau of Ships' method, which is a pyrolytic procedure at 900° C. in a current of dry hydrogen. The carbon is then burned in a stream of oxygen and is measured by absorbing the carbon dioxide in Anhydrone and Ascarite. The method is applicable not only to natural rubber but also to Buna S, the nitrile rubbers, and the vinyl polymers and copolymers. The British Standards Institution (45) also uses a method involving the measurement of the carbon dioxide formed from the combustion of the carbon black. Users' Memorandum No. U.9A (43) also recommends this procedure if clay or fillers are present which contain combined water.

Louth (130) has devised a method for the determination of carbon black in vulcanized rubbers which he claims is general for natural and all types of synthetic rubbers. For decomposition of the rubber he uses 1,1,2,2-tetrachloroethane and nitric acid. The often-encountered difficulty of filtering off the carbon black was overcome by the use of ether to coagulate the carbon particles. No empirical correction factor is required in this procedure and an accuracy of better than 0.5% is claimed.

Hammond (89) devised a method for determining the presence of titanium in the ash of a rubber vulcanizate.

A solution of the sodium salt of chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) is added to a sulfuric acid solution of the ash. A brownish-red to purple color develops if titanium is present. Mercury, silver, uranium, and ferric iron interfere with the test. A second test for titanium is the addition of hydrogen peroxide to the ash, which produces a golden yellow color if the element is present. Vanadium interferes with this latter test.

AGE RESISTORS AND ACCELERATORS

Chemists at the R. T. Vanderbilt Co. (12, 16) have compiled and described spot tests and other chemical tests for the identification of antioxidants and accelerators used in rubber. Deal (61) describes five spot tests and four test-tube reactions for the detection and identification of eight commercial antioxidants. Some of these tests are discussed for the first time. Accelerators may interfere and therefore the identifications may not be conclusive if made on vulcanized samples of rubber. Burchfield and Judy (50) describe color reactions obtained from amine antioxidants. The colors are produced mainly by coupling and oxidation reactions in organic solution in the presence of anhydrous stannic acid. They may be applied to the isolated material or to extracts of rubber. The tests cover a wide variety of antioxidants.

Schaefer (184) shows that it is possible to detect and identify the more generally used accelerators by means of color reactions. His tests can be used with mixtures of accelerators and also for vulcanized stocks. Proske (166) in 1940 did some preliminary work on the use of the polarographic method for the qualitative and quantitative analysis of organic accelerators of vulcanization. Surprisingly, there seems to have been no further research work done since that time on polarographic methods as applied to rubber analysis.

Dufraisse and Jarrijon (68, 103, 104) applied ultraviolet spectroscopy to the analysis of rubber products, especially to the accelerator tetramethyl thiuram disulfide. Dufraisse and Houpillart (67) analyzed several other accelerators by this method in a study of accelerator reactions during the vulcanization process. Kaye (107) reviewed the use of ultraviolet spectroscopy as applied to rubber. The method should be particularly useful for the determination of accelerators and antioxidants because of their intense absorption bands in the ultraviolet.

Katchalsky and Wechsler (106) determined catalyst fragments in synthetic polymers by the absorption of ultraviolet light. They studied benzoyl peroxide and acetyl peroxide. Banes and Eby (20) developed a rapid and accurate method for determining quantitatively some stabilizers in synthetic polymers by the method of ultraviolet absorption. The method is especially desirable when the stabilizers are present in very small concentrations and is more reliable than the chemical methods. They studied phenyl-β-naphthylamine and several other stabilizers in GR-S, in Butyl, and in the nitrile-type synthetic rubbers dissolved in various solvents. Rubber Reserve adopted the ultraviolet method (156) for the determination of stabilizers in GR-S and in GR-I.

Bellamy, Lawrie, and Press (23, 36, 165) applied chromatographic analysis to rubber compounding ingredients and their identification in vulcanizates. This method of selective adsorption separates the wax, fatty acids, accelerators, antioxidants, etc., from the rubber and from each other. After the quantitative separation of the accelerators and antioxidants, other means such as spot tests and ultraviolet absorption are used to identify or estimate them quantitatively. The authors applied the procedure to five different accelerators and to nine different antioxidants.

EVALUATION OF AGING BY OXYGEN ABSORPTION

Aging characteristics of natural rubber are usually determined by loss in tensile strength when the rubber is subjected to conditions that accelerate deterioration. This method has not proved entirely satisfactory for synthetic rubber vulcanizates (91).

Recently there has been considerable interest in the aging method employing chemical absorption of oxygen. Van Amerongen (9) modified an older method of Dufraisse (66) so that the absorption of oxygen would take place at any fixed pressure, thus enabling the amount of oxygen absorption to be measured directly in absolute terms. Carpenter and Twiss (52, 53) used a similar procedure in the investigation of a method for measuring the resistance to oxidation of a rubber. Traps were added to absorb the carbon dioxide and other gases which were formed, thereby preventing a dilution of the oxygen gas in contact with the rubber. Carpenter (52) includes in his article a good historical review of previous work done on this type of aging. Other investigators (37, 128, 147) have made improvements in design of the apparatus.

Stafford (198) described an experimental procedure for measuring the oxygen absorption of vulcanized rubber either in darkness or under illumination from a controlled source of light. He used a stainless steel oxidation cell previously developed by Harrobin, New, and Taylor (92). Albert (1) and Winn and Shelton (188, 238, 239) compared the oxygen absorption aging method with natural and artificial aging and found good correlation between them; thus they demonstrated the value of the chemical method.

MISCELLANEOUS

Volatile Matter. In crude natural rubber the only volatile material is moisture, which is usually determined by drying in an oven but sometimes by the xylene distillation method or by the Karl Fischer titration. A commercial moisture detector (11) makes use of electrode needles forced into the sample and the moisture content is read from a dial. The meter is said to be applicable to rubber. Hartshorn and Wilson (93) have developed a moisture meter which applies a constant alternating current to the sample in a small vessel, which may be regarded as a fixed air condenser, and the current passing through the sample is measured by a sensitive thermionic ammeter which can be adjusted to read the capacitance current (proportional to the dielectric constant of the material), the conductance current (proportional to its alternating current conductivity), or some function of both of these currents. Another commercial moisture detector (10) is claimed to have an accuracy of 0.1% in the range from 0 to 10% of moisture. The meter operates electrically and a measurement can be made in 2 minutes. Thus far, Rubber Reserve has not found a satisfactory meter for determining the moisture content of synthetic rubbers.

The specification for GR-S (156) requires that the volatile matter be determined by passing the rubber between the heated rolls of a laboratory mill. This removes not only moisture but also any monomer or other volatile material present in the rubber. In one sample of GR-S tested at the National Bureau of Standards a considerable amount of volatile material was formed while on the hot mill by the decomposition of the stabilizer. In this particular sample the moisture was then determined by the distillation method.

Polystyrene. Kolthoff, Lee, and Carr (118) developed a method for determining the percentage of polystyrene in GR-S which depends upon the degradation of GR-S by tert-butyl hydroperoxide in the presence of osmium tetroxide. Polystyrene is not attacked and is separated by precipitation with ethanol.

Mercury. Luke (131) determined small amounts of mercury in rubber containing iodine. The iodine is separated from the mercury, and the mercury determined by the Volhard method.

Selenium and Tellurium. Because of the increased use of selenium and tellurium as vulcanizing agents the R. T. Vanderbilt Co. (14) developed procedures for their quantitative determination. The two metals are oxidized to their acids by means of nitric acid and then separated by means of selective precipitation with sulfur dioxide.

Hydroperoxides. Laitinen and Nelson (124) worked out a

procedure for the determination of hydroperoxides in synthetic rubber. The peroxide is allowed to react with ferrous iron in benzene-methanol solution using o-phenanthroline as color reagent for excess ferrous iron. The results are good to about 20%. The method is sensitive to 10 to 20 p.p.m. of active oxygen. Phenyl-β-naphthylamine interferes with the reaction but this interference can be prevented by the addition of phosphoric acid. Robey and Wiese (178) determine the quantity of peroxides in synthetic rubbers by adding ferrous thiocyanate reagent to a benzene solution of the polymer and comparing the resulting color with that of a standard solution. Phenyl-β-naphthylamine does not interfere with this test. The method can detect as little as 10 p.p.m. of active oxygen and has an accuracy of 5 to 10%.

Crystallinity. Field (75) has developed a method for using the intensities of x-ray diffraction spots relative to that of the amorphous halo to determine the percentage of crystallinity in rubber specimens. He has obtained values of about 80% under the most favorable conditions. Goppel (84) has criticized the method and has made some modifications and alterations in it. He obtains values only about half those of Field.

Polarographic Methods. Proske (168) describes the polarographic methods of analysis in the rubber laboratories. This type of analysis is performed in a minimum of time and with a high degree of precision. Its chief use would be for the qualitative and quantitative analysis of compounding ingredients in a rubber sample and for trace elements.

Technical Microscopy. Allen (3) describes the application of technical microscopy as a useful procedure in the rubber industry. It can be used not only to determine particle size but also to supplement other methods for examining raw material, controlling factory processes, correlating physical properties with service performance, and solving factory difficulties.

Electron Microscopy. The most important function of the electron microscope in the rubber laboratory is the examination and evaluation of particle size and shape of reinforcing fillers (122). Several recent articles (88, 94, 109, 245) describe the methods of preparation of samples for use with the electron microscope and the possible applications of the new instrument in the rubber industry.

Statistical Methods. Several articles (46, 47, 87, 95, 141, 149, 154, 182, 192, 221) have appeared on the use of statistical methods in the evaluation of rubber. Information is given on their application to quality control, specifications, test methods, and design of experiment. Although most of these references describe the use of statistical methods as applied to physical measurements, they are also applicable to chemical measurements. It is anticipated that statistical methods will become a commonplace tool in the chemical rubber laboratory of the future.

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WATER ANALYSIS

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PROBABLY the most important advance in methods of analysis as applied to water chemistry during the past few years is the widespread adoption of instrumentation. Instead of relying on the human eye for the comparison of colors in colorimetric analysis, most laboratories now employ various types of electrophotometers. Indicators for determining pH are almost entirely replaced by electronic meters that are much more accurate and dependable. The tedious gravimetric methods for the alkalies have been replaced to a considerable extent by flame photometers. Until recently, however, commercial flame photometers were not susceptible of the precision and accuracy desired by the average analyst.

The next most outstanding advance in water chemistry is the introduction of a large number of organic reagents that are specific for the quantitative determination of inorganic constituents. This is also true of many other materials besides water. Some of these reagents are expensive and hard to obtain, but the advantages that accrue from their use make it fairly certain that they will become more generally available.

The ninth edition of "Standard Methods for the Examination of Water and Sewage" (5) contains many of the newer methods of analysis that have been developed during the past few years.

National associations have technical committees which are primarily concerned with improved and reliable methods for the chemical analysis of constituents and properties of water; included in this group are the American Society for Testing Materials, the American Society of Mechanical Engineers, and the Association of Official Agricultural Chemists.

Many of the new analytical procedures that have been described in the chemical literature have not been applied to the determination of constituents found in water. It may be that some water laboratories have adapted these procedures to their needs but have not yet published them. This review is concerned only with those methods developed during the past five years as applied to water analysis and reported in the technical literature.

SILICA

Photometric determination of silica is rapidly replacing the time-consuming gravimetric method. Most procedures as

applied to water and reported in the literature during the past 5 years have been based primarily upon the development of color with molybdate. Sax (121) used a quartz spectrophotometer to measure the yellow silicomolybdate complex produced. According to Bunting (24) and Straub and Grabowski (130) as little as 0.02 p.p.m. of silica can be determined in condensed steam or other water in the presence of phosphate by the destruction of phosphomolybdate with an organic acid and the reduction of silicomolybdic acid with 1-amino-2-naphthol-4-sulfonic acid reagent under pH control, forming molybdenum blue which can be read in any suitable photometer. Silica can be determined in the absence of phosphate (59) by the controlled reduction of phosphomolybdate and silicomolybdate with sodium sulfite by hydroquinone. The molybdenum blue coloration was measured on a Spekker absorptiometer (with Ilford red filter No. 608). Most of these colorimetric procedures require about 30 minutes and are reported to compare favorably with gravimetric analyses. In boiler water samples Teichert (140), using essentially the same method, obtained results that agreed within 0.05 mg. of silica by determining the absorption exactly 1 minute after the addition of sodium sulfite.

ALUMINUM AND IRON

As with silica, the colorimetric determination of aluminum is more rapid and apparently more accurate for low concentration than gravimetric methods. Strafford and Wyatt (129) found it desirable to have a method for determining 0.005 to 0.1 p.p.m. of aluminum in treated water. They found that both aurin tricarboxylic acid and hematoxylin colorimetric procedures were satisfactory; the latter was more convenient and of slightly greater sensitivity. Iron, an interfering ion, was removed by extraction of ferric thiocyanate with amyl alcohol and ether in the presence of a little hydrochloric acid. These procedures have been modified so that 0.1 to 0.5 p.p.m. of aluminum can be determined within 0.01 p.p.m. Experimental work on the determination of aluminum in water by means of hematoxylin has also been published by Houghton (62, 63).

Although the thiocyanate procedure for the quantitative determination of iron has been used for a long time, there is still some disagreement about its use in water analysis. Hallinan (57) has reported some advantages in a modified technique using relatively strong hydrochloric acid and potassium thiocyanate solutions. In boiler water analysis Teichert (140) made an extraction with amyl alcohol–amyl acetate mixture immediately after ammonium thiocyanate was added to the sample. The amount of light absorption was then measured. Lieffrig (76) has devised a shortened procedure for the determination of ferrous iron with dimethylglyoxime by adding sodium hyposulfite instead of hydrazine sulfate to reduce the ferric iron. o-Phenanthroline (25) reacts with ferrous iron (pH range 2.0 to 9.0) to form a highly colored orange-red product which can be measured photometrically. There is little interference with this method, and it is sensitive to 0.05 p.p.m. of iron. The results were 10% lower than with the thiocyanate method. Kuchment and Gengrinovich (71) used cacotheline, a nitro derivative of brucine, as an indicator in the titration of trivalent iron with stannous chloride solution. The percentage error ranged from 0.03 to 0.26.

CALCIUM, MAGNESIUM, AND HARDNESS

The standard volumetric procedure for determining calcium by precipitation with oxalate and titration with permanganate has been adapted by Scott and Johnson (125) by adding an excess of permanganate and measuring the residual color in a modern photoelectric colorimeter or spectrophotometer. From 0.3 to 3.4 mg. of calcium were determined by this procedure. A method for the colorimetric determination of calcium, reported by Barreto (14), depends on the difference in color corresponding to the amount of chloronilic acid which combined with calcium to

form an insoluble precipitate. Kuchment (71) utilized cacotheline, a nitro derivative of brucine, as an indicator in the direct titration of calcium salts with sodium oxalate. Potassium oleate–Duponol reagent (119) can also be used in determining the calcium content of water. The per cent of light transmission is measured against a blank, using a Corning No. 511 filter. Calcium concentrations from 3 to 140 p.p.m. can be determined with an average error of about 4%.

Magnesium may be determined photometrically by the method of Ludwig and Johnson (77) with 0.05% solution of Titan yellow in 2% Duponol. Total hardness is calculated from the calcium and magnesium.

The molybdate method of separating calcium and magnesium has been adapted to the determination of small amounts of calcium in water. As reported by Gandolfo (46), the optimum conditions for precipitation of calcium as molybdate were determined, and molybdenum in the precipitate was measured photometrically as the orange-red ether-soluble complex K_2 [MoO(SCN)$_6$] formed when calcium molybdate was treated in hydrochloric acid with potassium thiocyanate and stannous chloride. Moser and Robinson (92) also reported that it is possible to determine gravimetrically small quantities of the alkaline earths as normal molybdates.

McCoy (83) has described a procedure for determining small concentrations of calcium and magnesium by titration with a standard soap solution. The total hardness is first obtained by the standard Clark procedure, then the calcium is determined by the modified soap method of Polsky and Feddern (83). The difference between the two results is the hardness due to magnesium. Although the method was developed for water samples with a low concentration of calcium and magnesium, it is reported to give equally good results on hard water.

Bengolea and Amato (17) have confirmed Mendelaharzu's observation (87) that aluminum and silica interfere with the determination of magnesium by the Titan yellow method of Ludwig and Johnson (77). In analyses made by Bengolea and Amato, aluminum was removed by filtration at a suitable pH and special calibration curves were developed for magnesium in the presence of various concentrations of silica, resulting in a magnesium error of ±5%. Calcium up to 14 mg. per 100 ml., chloride up to 500 mg. per 100 ml., and organic matter did not interfere.

A variety of other methods for determining water hardness, such as ammonium purpureate (123), tropeolin 00 (39), and soap (9, 10, 93, 141) have been discussed in recent literature.

SODIUM AND POTASSIUM

The increasing importance of having accurate analytical values for sodium and potassium has placed a premium on more rapid procedures for these elements. The flame photometer has been further developed and improved, so that reliable instruments are now available for making accurate determinations. The time required for analyzing water for sodium and potassium is only a fraction of that required by older methods.

One of the earlier instruments and its application to the determination of sodium and potassium were described by Barnes et al. (13). The instrument was greatly improved by employing a dual optical system and internal standard (19). Improved units for intake of solutions have also been described (95, 143).

A nephelometric method for determining potassium using sodium cobaltinitrite was described by Kriventzov (70).

COPPER

Dithizone reagent was used by Buch (23) to determine the amount of copper and zinc present in waters of the Baltic Sea. Control of pH is an important factor in this procedure. Sodium diethyldithiocarbamate solution can be used to detect as little as 0.01 p.p.m. of copper with an error of about 5% (128). Golubeva

(53) has varied this method so that interference from iron, aluminum, zinc, lead, and coloration is prevented. Galtsoff (45) has applied the carbamate method to the analysis of sea water.

ALKALINITY

The methyl orange end point is frequently a difficult one to detect, especially by water plant workers untrained in chemical procedures. For years chemists have been searching for a suitable indicator with a sharper end point. Taras (135) proposes the use of two new total alkalinity indicators of the disasostilbeneaminedisulfonate series: disodium 4,4'-bis(o-tolyltriazeno)-2,2'-stilbenedisulfonate, and disodium 4,4'-bis(p-dimethylaminophenylazo)- 2,2'-stilbenedisulfonate. Unfortunately, these two indicators are unavailable on the chemical market, but directions are given for their preparation. The dyes of the stilbene group are advantageous for use in industrial work because they register a color change in the pH region between 4.0 and 5.0. In a later paper Taras (138) describes two other indicators of the stilbene group which register a color change immediately above pH 4.6.

For the preparation of a more stable methyl red indicator solution, Fleisher (44) suggests that instead of dissolving in alcohol, alphazurine be mixed with methyl red sodium salt and dissolved in distilled water.

Anderson and Robinson (6) have calculated "empirical coefficients" on the basis of glass electrode pH measurements of solutions to which known amounts of dilute hydrochloric acid have been added, and they have determined with an accuracy of about 1% the normality of a dilute solution of sodium bicarbonate containing a mixture of salts. The method described by these authors is for determining the alkalinity of sea water routinely, but it could be made applicable to other waters and fluids. Furthermore, a pH meter could be scaled to read normality, molarity, or alkalinity directly.

SULFATE

In the past few years there has been a considerable amount of experimental work done on the use of the chromate and dichromate ions for determining sulfate. Lupin (78) proposed a method in which water was treated with a measured volume of barium chloride, and the excess barium determined by adding alkaline dichromate to precipitate barium chromate and titrating the excess dichromate ions iodometrically. In a later article (79) Lupin suggested substituting ferrous sulfate solution in the presence of diphenylamine as an indicator for the more expensive potassium iodide. Nau (97) and Cantino (27) also utilized the iodometric titration, but they precipitated the sulfate by addition of barium chromate to an acidified water sample and eliminated the excess barium by making the solution alkaline. Cantino found a deviation of 0.2 to 1.2% from gravimetric analyses. A method described by Vorob'ev (148) is based on the potentiometric titration with potassium chromate of the excess barium ions remaining after the precipitation of sulfates. The experimental error did not exceed 1% when the quantity of sulfate exceeded 5 mg., but occasionally reached 5% when the quantity of sulfate ions in the sample was less than 5 mg.

A new procedure (146) for the iodometric determination of sulfur in mineral and medicinal waters has been reported. The sample of water is added to a mixture of measured amounts of potassium iodate, potassium iodide, alcohol, and starch solution saturated with sodium chloride until the solution is colorless. Each milliliter of standard potassium iodate solution is equivalent to 0.08 mg. of sulfur in the form of compounds encountered in mineral waters.

Although widely known, Noll's (99) description of the tetrahydroxyquinone method is worth mentioning. A neutralized sample of water is titrated with a barium chloride solution in the presence of isopropyl or ethyl alcohol, using tetrahydroxyquinone as an indicator. This method is not suitable for determining

concentrations of sulfate below 10 p.p.m. Chloride, silica, sulfite, tannins, and soluble salts of magnesium, calcium, and iron do not interfere. If phosphates are present bromocresol green is used instead of phenolphthalein when neutralizing.

Rybnikova and Bal'zamova (118) report that pure solutions of sulfates can be titrated conductometrically with barium acetate in an alcoholic solution when the concentration of sulfate ions is higher than 15 mg. per liter, and that sulfate in natural waters can be determined by the conductometric method if the concentration of chloride does not exceed 20 to 25 mg. per liter.

Satisfactory results were obtained by Anderson and Revelle (8) by the use of an electrical apparatus suitable for conductometric titrations. The instrument is so constructed that it registers conductance changes automatically. The titration was made with standard barium nitrate solution. When precipitation was controlled by seeding, as little as 1 mg. of sulfate could be determined within ±1% even in the presence of more than 50 times as much chloride, and the titration time required was only 5 minutes.

Small quantities of sulfate were determined turbidimetrically by Volmer and Frohlich (147). Glycine solution, gum arabic, and barium chloride were added to the water sample, and the turbidity was measured in a photometer with a selenium cell.

Goehring and Darge (50) found that if a solution is filtered through a synthetic resin the interfering ions, calcium, iron, and chromium, are removed and sulfate in the filtrate can be successfully precipitated with barium as pure barium sulfate. Good results were obtained with an ordinary zeolite ion exchanger for the removal of alkaline earth ions, and with an organic ion exchanger in eliminating chromic ions followed by a palmitate titration for determining the sulfate present (51).

Other papers that may be of interest to some analysts concern the determination of sulfate as sodium dehydroisoandrosterone sulfate in water and urine (132), and the determination of sulfate by means of sulfonated coal (69).

CHLORIDE

Rapid colorimetric methods for chloride, based on the suppression of the chloride ion in reactions between mercurous mercury and diphenylcarbazide have been reported by Sturz (131) and Lur'e and Nikolaeva (81). The minimum detectable concentration of chloride was found to be 0.025 p.p.m. A study was also made by Lur'e and Nikolaeva on a chromate diphenylcarbazide method, which was reported to be as accurate but more cumbersome than the mercurous mercury method.

An oxidimetric microtitration method for chlorides reported by Leithe (75) can be adapted to determining as little as 0.04 mg. of chloride in 5 ml. of drinking water. It consists basically of titrating chromate ions with ferrous sulfate in the presence of diphenylaminosulfonic acid as an indicator.

Application has been made of conductometric titration equipment to the determination of chloride in sea water and marine sediments (7). Although the time required per sample was doubled, the precision obtained was 0.01% or 5 times that by the standard Knudsen titration. Mikhlin (88) used a droppingmercury electrode in the polarographic determination of chloride and other halides.

FLUORIDE

For several years zirconium-alizarin methods have been recognized as the most satisfactory for determining fluoride in natural waters. Other zirconium reagents are also reported.

In 1943 Jendrassik and Papp (66) published a new procedure using zirconium hematoxylin in slightly oxidized state and fixed by acidification. This reagent must be kept air-free over carbon dioxide and stabilized by hydroxylamine hydrochloride.

A solution of ZrO^{++} reacts with purpurin to form a stable, violet-red lake which is bleached by fluoride ions. Jaki (65)

utilized this reagent for the determination of small quantities of fluoride in plants and mineral waters. The color was measured in a microphotometer. The results ran consistently higher by this method than had formerly been found, but in tests with known quantities of fluoride excellent agreement was obtained.

A method for determining fluoride has been described by Monnier, Rusconi, and Wenger (89) which is based on the fact that fluoride will bleach the violet color produced when ferric iron is added to 5-sulfosalicylic acid.

Lamar (73) reported a modified zirconium-alizarin method for the colorimetric determination of fluoride in water. This method embodies a stable acid indicator solution, the maximum suppression of the interference of sulfate, a sensitive color range, and a more accurate and convenient procedure. The acid indicator has a sensitive color range of 0.0 to 0.16 mg. of fluoride or 0.0 to 1.6 p.p.m. when 100 ml. of sample are used. Other workers (139, 149) have published additional information in regard to the zirconium-alizarin method of fluoride determination. Results accurate to 0.1 p.p.m. of fluoride have been obtained on a 100-ml. sample using a thorium-alizarin lake (133).

NITRATE AND NITRITE

Organic reagents are used almost entirely for the determination of nitrates in water. All the newer methods depend on the development of characteristic colors which are measured photometrically or spectrophotometrically.

Brucine reagent has been found to be very satisfactory for the determination of nitrate, especially in boiler waters. Noll (98) reported that there was no temperature interference from 20° to 80° C. and the color developed remained stable for at least 1 hour. Except for high color concentration which was easily overcome by dilution, the procedure was not affected by ions normally present in boiler waters. In 0 to 50 p.p.m. range of nitrate concentrations, an accuracy of approximately 0.5 p.p.m. was obtained. A photelometer, equipped with 1-cm. focused cells and a No. 1 blue filter, was used by Wittenburg and Crowell (152) for color comparison in the phenoldisulfonic method (5). Allerton (3) determined 50 to 200 micrograms of nitrogen as nitrate in water by heating the sample with Devarda's alloy and 0.1 N sodium hydroxide. A 50-ml. sample was distilled and the ammonia determined by Nessler reaction.

Zwicker and Robinson (155) have made a study of a photometric determination of nitrate in sea water using strychnidine reagent. A triturated mixture of 1-naphthylamine, sulfanilic acid, and powdered zinc was reported to be a suitable reagent for determining nitrate in water (86).

Studies have been carried out by Rider and Mellon (113) with General Electric recording spectrophotometer and Beckman spectrophotometer to ascertain the best procedure for determining nitrite by reddish purple coloration produced with sulfanilic acid and 1-naphthylamine. They found that diazotization should be carried out in strongly acidic solution; solution should be as cool as possible; coupling should not be attempted until diazotization is complete; and coupling should be carried out at as high a pH as is convenient with colorimetric stability. Whitehead (150) reports that the Evelyn photoelectric colorimeter can be used with the 1-naphthylamine method for nitrites, provided sufficient time (60 minutes) is allowed to elapse between additions of sulfanilic acid and 1-naphthylamine to sample permitting initial diazotization to reach completion. Alzamoro (4) reports that the azo compound made from xylidine and 2-naphthol is stable, sensitive (0.028 mg. of nitrite per liter), and gives a stable color with acceptable accuracy over a wide range of concentrations.

PHOSPHATE

A procedure for phosphate determination in boiler waters in the absence of tannin, and various methods for overcoming its interference, have been described by Goldman and Love (52). The interference was eliminated by potassium nitrate coagulation,

potassium persulfate bleach, and tannin removal by decolorizing carbon. The latter was considered the most convenient. Phosphomolybdic acid can be reduced to molybdenum blue by adding Rodinol (a photographic developer containing p-aminophenol as a reducing agent) or Rullex [a developer containing substituted aminophenol (140)]. When the absorption reaches a constant value, comparison can be made with standards. Remp (110) used a volumetric method for determining phosphate based partially on the gravimetric analysis outlined in (5).

DISSOLVED SOLIDS

A method for determining total solids in mineral waters, brines, and other salt solutions that undergo partial decomposition on heating has been reported by Tananaev and Levina (134). The brine sample is added to a dry, weighed amount of sodium fluoride, and the sodium fluoride is reweighed, then dried to a constant weight. Maguire and Polsky (85) have shown gallic acid to be preferable to sulfuric acid as a neutralizing medium in measuring conductance of boiler water when determining dissolved solids.

RESIDUAL CHLORINE

A method for determining free chlorine with benzidine has been reported by Olszewski (101). However, the o-tolidine test, with numerous variations, is still the most widely used. o-Tolidine-p-aminodimethylaniline (90, 91, 102) has been used as an indicator in the study of chlorine and ammonia treatment. The "flash" p-aminodimethylaniline test for chlorine and the oxidation-reduction potential determination are believed by Moore (91) to be the most sensitive and reliable indicators of the breakpoint in the chlorine-ammonia reaction. Results obtained are usually accurate to 0.02 p.p.m. (102). Chamberlin and Glass (29, 30) have described a method with special reference to concentration, pH, effect of adding reagent, preparation of o-tolidine, and temperature of chlorine standards. This study has resulted in a more rapid color formation, increased stability, and less interference due to iron and nitrate. Free available chlorine can be titrated with a standardized o-tolidine solution (34) with approximately the same precision as the iodometric titration or the o-tolidine-arsenite colorimetric tests. Nitrates, ferric iron, manganic manganese, chloramines, and turbidities as high as 400 p.p.m. cause no serious difficulties. The o-tolidine-arsenite (48, 49, 58, 61) test is considered a quantitative method for differentiation of active chlorine from chloramine, and interference from manganese, nitrite, and iron seems to be eliminated.

Taras (136, 137) has presented a colorimetric method of determining free chlorine with methyl orange. It is based upon the fact that there is a definite reaction between free chlorine and methyl orange which occurs in the ratio of 2 moles of free chlorine to 1 mole of the dye.

The details of four amperometric titrations with sodium arsenite have been reported by Haller and Listek (56) in which water may be analyzed for free available chlorine, chloramine, chlorine dioxide, and chlorite separately and expressed as residual available chlorine in the order of fractional parts per million.

The American Water Works Association Committee on Control of Chlorination has published a rather complete discussion of approved methods. Included are the o-tolidine, iodometric, chlorine and chloramine differentiation, and chlorine demand methods. These are not alternative procedures, but each has its place under certain conditions (26).

The use of an automatic device for recording residual chlorine in a public water supply system has been reported by Baylis et al. (16).

DISSOLVED OXYGEN

Practically all methods for determining dissolved oxygen that are in use today by water analysis laboratories are modifications of the Winkler test. The influence of temperature is one of the

factors that has come to the attention of analysts in recent years. Bond (*21*) found that erroneous results are obtained by the Winkler test if the titration is carried out at a temperature above 21° C. Because of the difficulty in cooling boiler water samples, Pinkney and .Young (*107*) recommended the use of a method not requiring starch as an indicator in determining low concentrations of oxygen. Instead, they used a procedure wherein the dissolved oxygen releases an equivalent amount of chlorine which can be measured colorimetrically with the aid of o-tolidine. A photoelectric absorptiometer (*11*) can be used for determining liberated iodine by measurement of intensity of the starch-iodide complex. Pomeroy and Kirschman (*109*) found that by increasing the quantity of iodide, the interference from organic matter was lessened and a sharper end point was produced. Another interesting study is that of Cusachs (*36*) on the Alsterberger azide modification for determining dissolved oxygen and the Platner (*108*) stable alkaline starch solution. A careful investigation of the Winkler method by Sillars and Silver (*126, 127*) showed that about 0.05 ml. of oxygen per liter of water can be determined with satisfactory precision provided certain precautions are taken. They recommend that multiple samples by analyzed, that electrometric and back-titrations be used, and that calculations be made by a series of formulas allowing for blanks. When an amperometric titration of iodine in small concentrations is used, satisfactory results from the Winkler method have been obtained (*42*).

The Department of the Navy (*1*) has developed details of apparatus, sampling, fixing, titrating, and calculation for both field and laboratory determinations of dissolved oxygen. The field method utilizes Winkler reagents, whereas the laboratory method requires electrometric titrations with the fixing reagent containing free iodine in an amount sufficient to combine with reducing impurities in the sampled water. The laboratory method gave values of dissolved oxygen with a precision of 0.001 p.p.m., and the field method measured the concentration with an accuracy of about 0.02 p.p.m.

Ellis and Ellis (*40*) used amidol in a rapid photometric method accurate to less than 0.1 p.p.m. in routine tests. Dissolved oxygen can also be determined with amidol by adding potassium citrate solution and comparing the color obtained with a standard cobaltous chloride solution (*151*). Nitrites interfere with this determination but can be corrected for by adding potassium dichromate. This method is said to be preferable to the standard Winkler method because it is simpler, speedier, and can be used in the field.

Leithe (*74*) determined dissolved oxygen in water without the use of a reagent containing iodine. He added an excess of a standard ferrous sulfate solution to the water sample and titrated the excess ferrous iron with a standard solution of potassium permanganate.

Traces of dissolved oxygen produce a bright yellow-green fluorescence with aqueous or alkaline solution of adrenaline, which in the absence of oxygen possesses a barely perceptible milky-blue fluorescence. The intensity of the fluorescence is proportional to the oxygen content. Konstantinova-Shlezinger and Krasnova (*67*) determined as little as 1.8 micrograms of oxygen per ml. by replacing the glass aperture in a König-Martens spectrophotometer with a quartz aperture.

Oxygen dissolved in sea water has been determined polarographically by Giguere and Lauzier (*47*) using a dropping-mercury electrode or a stationary platinum microelectrode in a concentration as low as 0.02 ml. per liter with a precision of 0.02 ml. per liter. Laitinen, Higuchi, and Czuha (*72*) have reported a simple, rapid, and sensitive potentiometric method for the determination of traces of oxygen based on the measurement of the null potential of a dropping-mercury electrode.

Ulmer *et al.* (*144*) have made a study of the applicability of the Schwartz-Gurney method for determining dissolved oxygen in boiler feed water and have modified the method to make it es-

pecially applicable in the presence of impurities encountered in power plants.

CARBON DIOXIDE

In the determination of free carbon dioxide in waters by titration with sodium hydroxide or sodium carbonate against phenolphthalein, recognition of the end point is made difficult by the presence of large quantities of calcium and magnesium salts and of ferrous bicarbonate. Interference by these substances can be prevented by adding an excess of 0.1 N sodium carbonate solution containing Seignette or Rochelle salt to the water and back-titrating with 0.1 N hydrochloric acid (*104, 106*). The color change of phenolphthalein takes place at a lower pH than corresponds to neutral calcium bicarbonate, so that the results obtained by the titration are frequently low. Papp (*105*) has set up a table to be used in correcting for this error. With the aid of this table and a titration with hydrochloric acid, Papp states that it is possible to determine very small quantities of free carbon dioxides.

McKinney and Amorosi (*84*) have reported a procedure with a precision of ±1 p.p.m. that they believe overcomes the defects in many of the other titration methods in use. It consists of titrating the water sample between two properly selected pH values, acidifying, boiling off carbon dioxide, cooling sample, and retitrating between the same two pH values. The difference between the two titrations gives the carbon dioxide in the sample.

Several methods (*35, 37*), based upon the precipitation of carbon dioxide as barium carbonate, have been reported in recent literature.

An improved evolution method was developed by Clarke (*33*) using a completely closed system for evolution and circulation of carbon dioxide which is absorbed in barium hydroxide; the residual hydroxide is titrated with standard acid. Precision and accuracy are excelled and time required is only 15 minutes per determination.

ORGANIC SUBSTANCES

In the determination of organic matter in water, Urbanowiczowna (*145*) found that potassium iodate gave more reliable results than potassium permanganate. Because of stability of the oxidizing agent itself and stability of the titers, Bezel (*20*) believes that cerium sulfate is superior to permanganate in sanitary practice. After an examination of the official methods for determining oxidizable substances in drinking water, Zheleznikova (*154*) developed an improved procedure using potassium permanganate.

A colorimetric method of determining phenols and naphthols, based on the color formed in the reaction of chloramine-T with phenols in aqueous solution, has been reported by Afanes'ev (*2*). A modified dibromoquinonechlorimide procedure by Basavilbaso (*15*) is direct, avoids distillation of the sample, and is said to be five times more sensitive than the procedure given in (*5*). Copper sulfate has been found to be the most effective preservative of phenol in waters (*41, 124*).

Since the practice of spraying whole communities with DDT has been initiated, it has become desirable to have a check on the extent to which open reservoirs are being impregnated with this compound. The xanthydrol–potassium hydroxide–pyridine method (*28*) can be used to develop a red color with DDT. Another colorimetric method (*122*) depends on the intensive nitration to polynitro derivatives of constituents of DDT and the production of intense colors upon the addition of methanolic sodium methylate to the benzene solution of the nitration products. A filter photometer can be used for the comparison, but the spectrophotometer is recommended.

In addition to the above procedures, methods of determining methane (*103*), furfural (*55*), petroleum products (*82, 100*), and tannin (*60*) have been published during the past five years.

MISCELLANEOUS

There are numerous other discussions of new methods and revisions of old standbys appearing in periodicals during recent years.

A modification of the d'Ans and Hofer method for determining traces of bromide in underground waters has been reported by Houghton (64). Ronco (115) has outlined a procedure for the determination of small quantities of bromide in the presence of large amounts of chloride. Bengolea and Raggio (18) have reported a potentiometric method of determining boron in which a 55% invert sugar solution is added to the sample and titrated with sodium hydroxide using a glass electrode.

Small quantities of copper, bismuth, lead, cadmium, and zinc in natural waters can be determined polarographically with a mean error of ±5% (111). A potentiometric method (38) for selenium has been adapted to the analysis of water.

By adding a little phenol and some alkaline hypochlorite solution to a water sample, ammonia can be determined with a photoelectric colorimeter. This test can be made in 6 minutes, and the results compare favorably with those obtained by the more tedious Kjeldahl procedure (153). Chirkov (31) determined inorganic ammonia by distillation in the presence of zinc oxide; protein ammonia was determined by distillation in the presence of calcium oxide and potassium permanganate solution. Nessler reagent was used for development of color.

Lur'e (80) has developed an accurate colorimetric method for determination of small quantities of thiocyanates in waste waters using pyridine. An improved phenolphthalein technique (114) serves to determine 0.5 microgram of cyanide in 2 ml. of solution with only about a 3% error. During the war the importance of detecting and quantitatively determining arsenic came into prominence especially in connection with the possibility of contamination of water supplies by poisonous gases. Various methods were discussed in the literature during those years (54, 117).

Of interest also has been the following wide variety of investigations in the field of water analysis: determination of deuterium in water by a mass spectrophotometric method (43); use of di-β-naphthylthiocarbazone in a direct method for zinc (116); use of the cylindrical colorimeter in measurement of pH (12); variations of the periodate method for manganese (68); polarographic determination of sodium and lithium (112); modernization of the B.O.D. test (120); photometric determination of water clearness (32); photocolorimetric hydrogen peroxide method (22); photometric lead method based on the formation of the lead-dithizone color complex (94); and improved methods for determination and calculation of threshold odor (96, 142).

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Determination of Gamma Isomer of Benzene Hexachloride

Mass Isotope Dilution Method

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A mass isotope dilution method for the determination of the gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane is described. Gamma-hexadeuterobenzene hexachloride is used as the tracer molecule and the extent of isotopic dilution in the isolated gamma isomer mixture is determined by means of infrared spectrophotometry. The extension of this method to the determination of alpha, beta, and delta isomers, although of less practical importance because of their entomological inactivity, is also discussed. The infrared absorption spectra of the alpha, beta, and gamma isomers of hexadeuterobenzene hexachloride over the range of from 2.5 to 15 mu are presented.

EVER since the discovery in 1943 by F. J. D. Thomas (*12*) of the insecticidal activity of the gamma isomer of benzene hexachloride, there has been interest in the development of reliable methods of assay for its determination, particularly in mixtures containing considerable amounts of the other four known isomers as well as other chlorination products of benzene.

Several methods of assay have come to the authors' attention. The first is based upon direct infrared spectrophotometry (*4, 8*). The second is a biological method involving the paralysis of 3-day-old mosquito larvae of *Ades aegypti* (*5*). The third is based upon a solubility method (*11*), and the last upon lowering of melting point (*2*). The reliability of all these methods is obviously dependent to a greater or lesser degree upon the nature and amount of the nonbenzene hexachloride material present in any given sample being assayed. Thus some commercial crudes give erroneous results when assayed by direct infrared spectrophotometry. Moreover, it has been observed that such "background" material exerts a very definite effect upon the solubility behavior of the gamma isomer (*11*).

In view of this situation the authors decided to appeal to an approach that is not subject to these defects and is, therefore, absolute in the sense that the reliability (accuracy) of the result is determined only by the precision of the technique used. Such an approach is offered by the isotope dilution method. The simplest isotopic tracer to obtain and to introduce into a molecule like benzene hexachloride is, of course, the stable isotope deuterium. Consequently the present assay method is based upon the addition of a known amount of γ-hexadeuterobenzene hexachloride to a known amount of the sample to be assayed (if the assay of any of the other isomers is required, the appropriate alpha, beta, or delta hexadeutero isomer may be added). The whole mixture is then dissolved to render it homogeneous and a specimen of the mixed (isotopically) gamma isomers is isolated. The ratio of $C_6H_6Cl_6$ to $C_6D_6Cl_6$ in this isolated specimen is then determined by direct infrared spectrophotometry.

PREPARATION OF HEXADEUTEROBENZENE HEXACHLORIDE TRACERS

There are two generally useful methods whereby deuterium may be exchanged for the protium in benzene. The first involves the use of deuterosulfuric acid (*7*); the second, catalytic exchange using deuterium oxide and a nickel catalyst at 200° to 300° C. (*3*). The second method was used.

To a mixture of 220 grams of purified benzene and 200 grams of (99.5%) deuterium oxide were added 1 to 2 grams of Raney's nickel catalyst (wet with benzene). The whole mixture was placed in a stainless steel hydrogenation bomb and after closing was heated at 250° C. with shaking until equilibrium had been

attained. The rate of reaction was followed by withdrawing small specimens of the benzene phase from time to time and examining their infrared absorption spectrum with particular attention to the magnitude of the C—H and C—D linear stretching frequencies at 3.26 and 4.36 mu, respectively. By this means it was found that about 60 hours were required to attain equilibrium. After cooling and separation of the phases, the partially deuterized benzene phase was returned to the bomb and treated with a fresh 200-gram portion of deuterium oxide and a fresh 1- to 2-gram portion of Raney's nickel catalyst and the 60 hour-heating period was repeated.

After five such treatments 195 grams of deuterized product were obtained. In order to determine the degree of deuterization of this material a small portion was purified.

Three grams of *trans*-4,4'-dihydroxy-α,β-diethylstilbene (diethylstilbestrol) were dissolved in about 40 ml. of the deuterized benzene and after standing for 17 hours at 23° C. the crystals of the benzene solvate of "diethylstilbestrol" were filtered off. The deuterobenzene was then recovered from this solvate by passing a slow stream of dried air through the heated (56° C.) crystals and collecting the deuterobenzene in an ice-cold trap. In this manner 1.2 grams of deuterobenzene free of cyclohexane, thiophene, etc., were obtained.

The infrared absorption spectrum of this purified product in the liquid state as determined on a carefully calibrated (*10*) Model 12A Perkin-Elmer infrared spectrometer was found to agree closely with that reported by Herzfeld, Ingold, and Poole (*6*) except for the presence of two moderately strong bands at 3.47 mu (3060 $\bar{\nu}$) and 14.05 mu (711 $\bar{\nu}$), neither of which was reported by the British workers. Because, however, the deuterobenzene used here is only 93 atom % deuterium while the British workers reported their deuterized benzene to be 99 atom %, it is possible that the 3.47- and 14.05-mu bands might arise from the 25 to 30 mole % of C_6D_5H present in the preparation. The authors were, however, unable to check this inference, since they have been unable to find infrared data for C_6D_5H. In determining the extent of deuterization of their product, they measured its density by means of a micropycnometer and computed the deuterium concentration from the density value for pure hexadeuterobenzene of $d_{25°}^{25°} = 0.94611$ given by Weldon and Wilson (*16*). For ordinary benzene they observed a density value of $d_{25°}^{25°} = 0.87580$ and for their deuterobenzene $d_{25°}^{25°} = 0.94108$. Combining these data with those of Weldon and Wilson they found that their benzene contained 93 atom % of deuterium, which they considered sufficiently good for their purposes.

The chlorination of the deuterobenzene was carried out as follows: One hundred and thirty nine grams of hexadeuterobenzene were treated with 150 grams of chlorine under a nitrogen atmosphere and irradiated by means of a G.E. sun lamp in a manner usual for photochlorinations. From this reaction 184 grams of crude benzene chlorination products were obtained and by fractional crystallizations in the usual manner (*12*) 12 grams of the pure gamma isomer of hexadeuterobenzene hexachloride (melting point 112.5° C.) were obtained.

A careful study of the melting point behavior of the gamma isomer to which small amounts of the other isomers had been

Table I. Infrared Absorption Bands

Wave Length, Microns

α-C₆D₆Cl₆	β-C₆D₆Cl₆	γ-C₆D₆Cl₆	γ-C₆H₆Cl₆
13.80 S[a]	14.28 S (broad)	13.77 S (broad)	14.90 S
13.67 S	13.00 W	12.83 W	14.50 S
12.91 M	12.56 W	12.69 M	14.21 S
12.70 W	12.30 W	12.54 W	12.80 S
12.55 W	11.67 S	12.26 M	11.77 S
12.38 M	10.10 M	12.20 M	10.97 M
12.20 W	10.00 W	11.97 M	10.50 M
11.95 M	9.72 S	11.80 W	10.34 W
11.84 M	9.37 M	11.27 S	10.28 W
11.22 M	9.10 S	10.93 M	9.94 W
10.91 S	9.05 S	10.60 M	9.75 M
10.55 M	8.72 M	10.37 M	9.06 S
10.43 W	7.96 M	9.62 W	8.41 M
10.33 W	4.46 M	9.55 S	8.20 W
10.11 S	3.41 M	9.18 W	8.08 M
9.89 S		8.88 S	7.96 M
9.61 S		8.47 S	7.77 M
9.36 W		7.88 W	7.40 S
9.24 W		4.46 M	3.41 M
9.10 S		3.41 M	
8.91 W			
8.84 S			
8.47 S			
7.89 W			
4.46 M			
3.41 M			

[a] S, M, and W indicate strong, moderate, and weak absorption intensities.

added has shown that the melting point is a very sensitive and reliable index of purity. The authors have observed that amounts of the alpha isomer added to the gamma isomer which are too small to be easily observed by infrared measurements are readily detected by the melting point behavior.

Specimens of some of the other isomers of hexadeuterobenzene hexachloride are, of course, also isolatable in pure form during the procedure for isolating the gamma isomer and these may be used in assaying for their respective isomers where required.

In Figures 1 to 4 and Table I are presented the infrared absorption spectra of α-, β-, and γ-hexadeuterobenzene hexachloride and of γ-hexaprotiobenzene hexachloride run as solid mulls in petrolatum. The infrared absorption spectra of the other known

protio isomers are not presented because spectral measurements for them agree in every detail with those presented by other workers (4, 9).

Table II is the slit schedule used in obtaining the above spectra.

SPECTROPHOTOMETRIC DETERMINATION OF ISOTOPIC DILUTION

A superficial inspection of the spectra of the two gamma isomers reveals that there are two intense absorption bands in each which are clearly suitable for use for the spectrophotometric determination of these substances. These are, for the solids, 14.51 and 11.74 mu for the protio isomer and 13.79 and 11.28 mu for the deutero isomer. In dimethyl formamide as solvent the corresponding absorption bands are shifted slightly and occur at 14.55 and 11.83 mu for the protio isomer and 13.75 and 11.21 mu for the deutero isomer.

It is, of course, possible to carry out the desired spectrophotometric analysis for the relative amounts of $C_6H_6Cl_6$ and $C_6D_6Cl_6$ using either solids or solutions, but as, in general, the authors have found solutions somewhat easier to manipulate, they have adopted them for regular use. Naturally, an involatile solvent is desirable for quantitative manipulation, and in looking about for a suitable one the authors found that dimethyl formamide has several properties which render it useful as a solvent for quantitative infrared spectrophotometry. Apart from its easy preparation and purification it has a high boiling, 153° C., and excellent general solvent characteristics (many sodium salts freely dissolve in it), and its infrared spectrum contains only one band (at 11.55

Table II. Slit Schedule

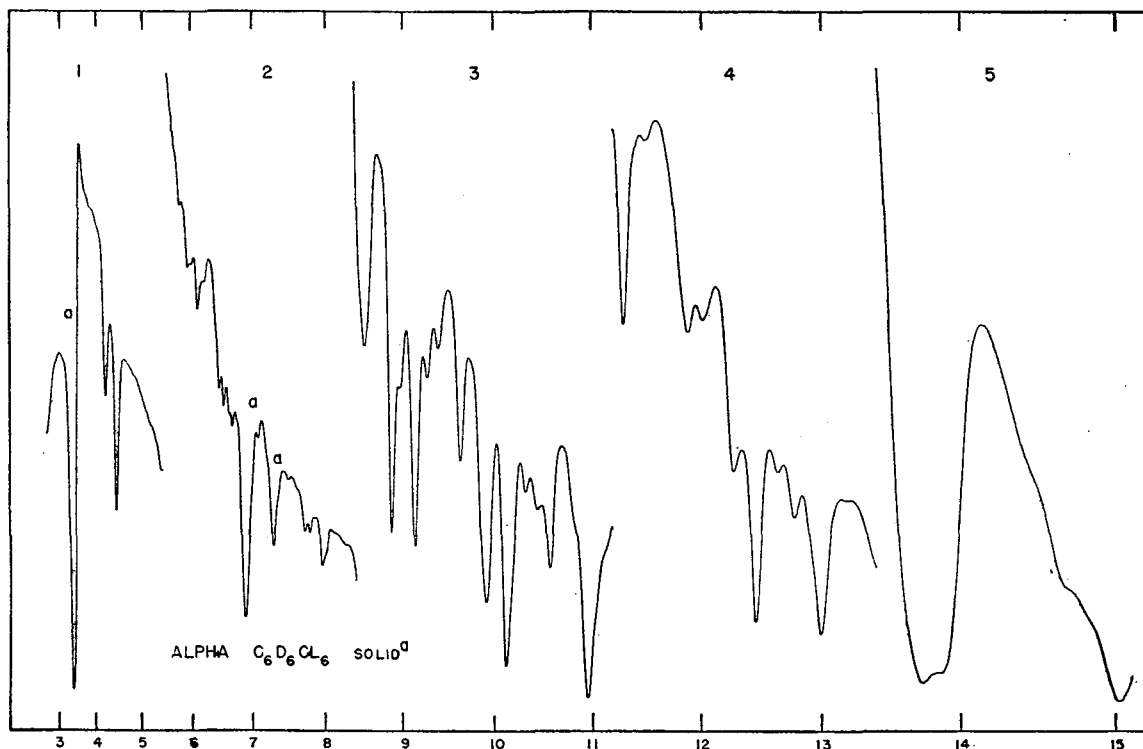| Spectrum Section	Slit Width, Mm.
1	0.100
2	0.150
3	0.300
4	0.500
5	1.00

Figure 1. Infrared Absorption Spectra

a. Bands due to petrolatum vehicle used in making absorption layers

Table III. Infrared Absorption of γ-Hexaprotiobenzene Hexachloride–γ-Hexadeuterobenzene Hexachloride Mixtures

% $C_6D_6Cl_6$, $f_{\gamma D}$	Optical Density	
	d (slit 0.900) 13.75 mu	d (slit 0.500) 11.83 mu
100	0.761	0.140
75	0.596	0.297
50	0.431	0.455
35	0.334	0.559
25	0.267	0.613
0	0.100	0.767

mu) between 10 and 15 mu. Where the direct infrared analysis of the benzene hexachloride isomers is required, dimethyl formamide has an added advantage over solvents formerly used in that the beta isomer, being freely soluble, may also be determined along with the other isomers.

The most suitable conditions for making the desired optical measurements are a constant concentration of 200 mg. of sample per ml. (948 mg.) of purified (redistilled, boiling point 153° C.) dimethyl formamide placed in a sealed absorption cell of 0.10-mm. path length. Through the use of these conditions and by making up a series of known mixtures of the protio and deutero γ-benzene hexachlorides, the optical densities of such mixtures could be determined at the 13.75- and 11.83-mu bands, using the empty cell as the reference state. In this manner the calibration data presented in Table III were obtained.

Beer's law is followed closely, as would be expected of such a system as that under study here. Similar calibration curves could be established for the other isomers if desired. In analyzing mixtures of the α-protio-α-deutero isomers the infrared absorption bands at 13.15 and 13.70 mu, respectively, could be used, while for the β-protio-β-deutero isomer mixtures the 13.5- and 14.35-mu absorption bands would serve. The authors have found that the absolute values of the calibration remain satis-

factorily constant, provided the optical density of the solvent is maintained constant. This is best achieved by preparing a large batch of dried and purified dimethyl formamide and, having established the calibration curve through its use, setting it aside exclusively for these isotope dilution assays. Water in the dimethyl formamide is the worst offender and should be carefully guarded against. If the solvent-filled cell rather than the empty cell had been used as reference state I, much of the effect due to change in the solvent characteristics could have been avoided, but because their procedure proved entirely satisfactory and is simpler of manipulation the authors preferred to use it.

ISOLATION OF PURE GAMMA ISOMER FROM TYPICAL CHLORINATION CRUDES

In carrying out an analysis by means of the isotope dilution method it is of first importance to be able to isolate qualitatively a typical specimen of the pure molecular species for which assay is required. After considerable experimentation the following process was developed for isolating a specimen of the pure gamma isomer (isotopically mixed of course) of benzene hexachloride.

About 15 grams of the crude sample are weighed out accurately and dissolved in a 50-ml. volumetric flask containing acetone. So large a sample is taken to ensure average uniformity, as benzene hexachloride crudes are sometimes inhomogeneous physically. Exactly 5.0 ml. (W_s) of the acetone solution are put into a suitable evaporation vessel and γ-hexadeuterobenzene hexachloride is added to the extent of about 15% of the weight of the dissolved crude (1.5 grams × 0.15 = 0.225 gram). This is weighed out exactly $(W_{\gamma D})$ and dissolved in the 5.0-ml. aliquot of acetone solution. This ensures uniform distribution of the γ-hexadeuterobenzene hexachloride throughout the sample.

The solution is evaporated to dryness to remove the acetone, then 5 ml. of petroleum ether are added to the residue to de-oil the crude. It is triturated at room temperature and finally in an ice bath for at least 5 minutes and filtered at once. The filtrate, which contains all the oil constituents of the crude (chiefly heptachlorocyclohexane), is rejected. The solid filter cake is placed in a flask equipped with a condenser, and is refluxed with 15 ml. of
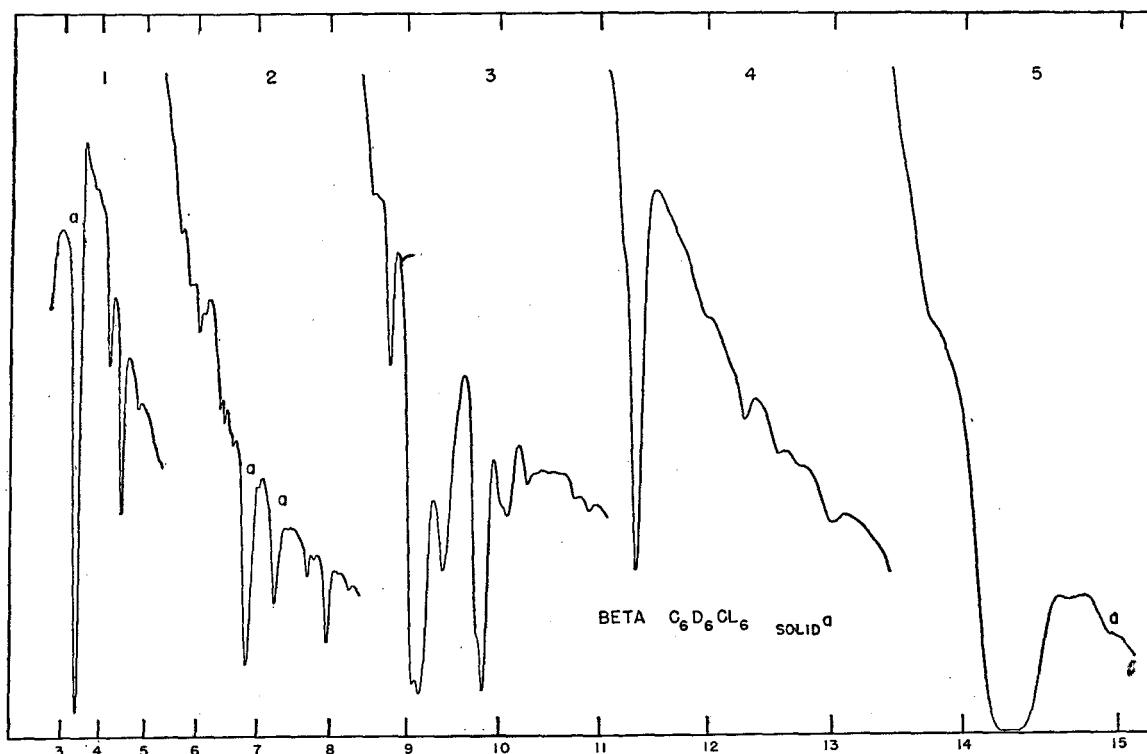

Figure 2. Infrared Absorption Spectra

a. Bands due to petrolatum vehicle used in making absorption layers

iso-octane for about 10 minutes to dissolve all the more soluble alpha, gamma, and delta isomers. The amount of iso-octane used should be based on a ratio of 0.1 gram of de-oiled sample per ml. This ratio has to be adhered to if pure gamma isomer is to be obtained at the end of this isolation procedure.

After refluxing, the flask is stoppered, put on a mechanical shaker, and shaken for at least 2 hours at room temperature. The solution is filtered and the filtrate evaporated to dryness on a steam bath. The residue weight at this point is usually between 0.35 and 0.40 gram, and its gamma isomer content is between 55 and 60% as determined by direct infrared spectrophotometry. This residue is crystallized from a 90% ethylene glycol–10% water mixture (by volume) as follows.

An amount of the latter "solvent" corresponding to 11 mg. of residue weight per milliliter is used and the system is heated on a steam bath with vigorous mechanical stirring until the solids are completely dissolved. The hot solution is filtered, seeded with a tiny crystal of the gamma isomer, and allowed to crystallize at about 5° C., being stirred only occasionally over no more than a 4-hour period. If longer periods are allowed, undesirably large amounts of the alpha isomer will be found in the solid. The crystalline solid is filtered and washed on the filter, first with a little of the ethylene glycol solvent and then with water until all the glycol has been removed. The solid is dried at 56° C. for about 1 hour in vacuo.

This product should be essentially pure gamma isomer and should have a melting point with a range no greater than from 108° to 112° C. to be of acceptable purity for the subsequent infrared measurements. This melting point range has been found to correspond to the presence of from 1 to 2% of the alpha isomer. If the product obtained does not meet this purity requirement it may be satisfactorily purified by recrystallization from isopropanol in the ratio of 190 mg. of product per ml. in the usual manner—i.e., dissolved on the steam bath and allowed to crystallize at room temperature. In this manner about 60 mg. of pure gamma isomer are obtained for the final infrared isotope dilution measurement as described above.

Most of the operations involved in the foregoing isolation procedure are so carried out as to avoid the attainment of thermodynamic equilibria for, in fact, if such equilibria were to be established the isolation of the pure gamma isomer would be impossible. It is, therefore, essential that the above procedure be followed in every detail.

If assays for the beta and alpha isomers are desired, a method for their isolation will be required. For these isomers, however, isolation is far more simple, inasmuch as the insolubility of the beta isomer makes its isolation practically a matter of simple filtration, while the fact that the alpha isomer occurs to the extent of 65 to 70% in the usual chlorination crude makes its isolation equally simple.

COMPUTATION OF RESULTS

As for any tracer dilution assay, the desired numerical result is computed from an equation of the following form:

$$F_\gamma = \frac{W_{\gamma D}\,(1 - f_{\gamma D})}{W_s f_{\gamma D}}$$

where

F_γ = fraction of gamma isomer in sample
$W_{\gamma D}$ = weight in mg. of added isotopic tracer
W_s = weight in mg. of sample containing $W_{\gamma D}$ mg. of tracer
$f_{\gamma D}$ = fraction of deutero isomer found in the isolated specimen

There are several possible ways in which the $1 - f_{\gamma D}$ and $f_{\gamma D}$ terms in the above equation may be evaluated.

First, since $1 - f_{\gamma D}$ is equal to $f_{\gamma P}$ (the fraction of the protio isomer) and the technique makes it possible to determine $f_{\gamma D}$ and $f_{\gamma P}$ as independent measurements at 13.75 and 11.83 mu, those two values could be introduced, as observed, into the equation and so a value for F_γ computed. Secondly and thirdly, one might elect to use either the $f_{\gamma D}$ or $f_{\gamma P}$ values, obtaining the $1 - f_{\gamma D}$ or $1 - f_{\gamma P}$ values by simple subtraction, and thus evaluate F_γ.

The selection of which of the three methods to use in order to obtain the greatest accuracy in the final result will, in general, depend upon a variety of circumstances associated with the nature of the impurity likely to be present in the isolated isotopically diluted specimen. Unless the isolated isotopically diluted specimen can be made entirely pure, it is very likely that the impurity will affect the infrared absorption at one wave length more than at another and consequently the most accurate value of F_γ will be
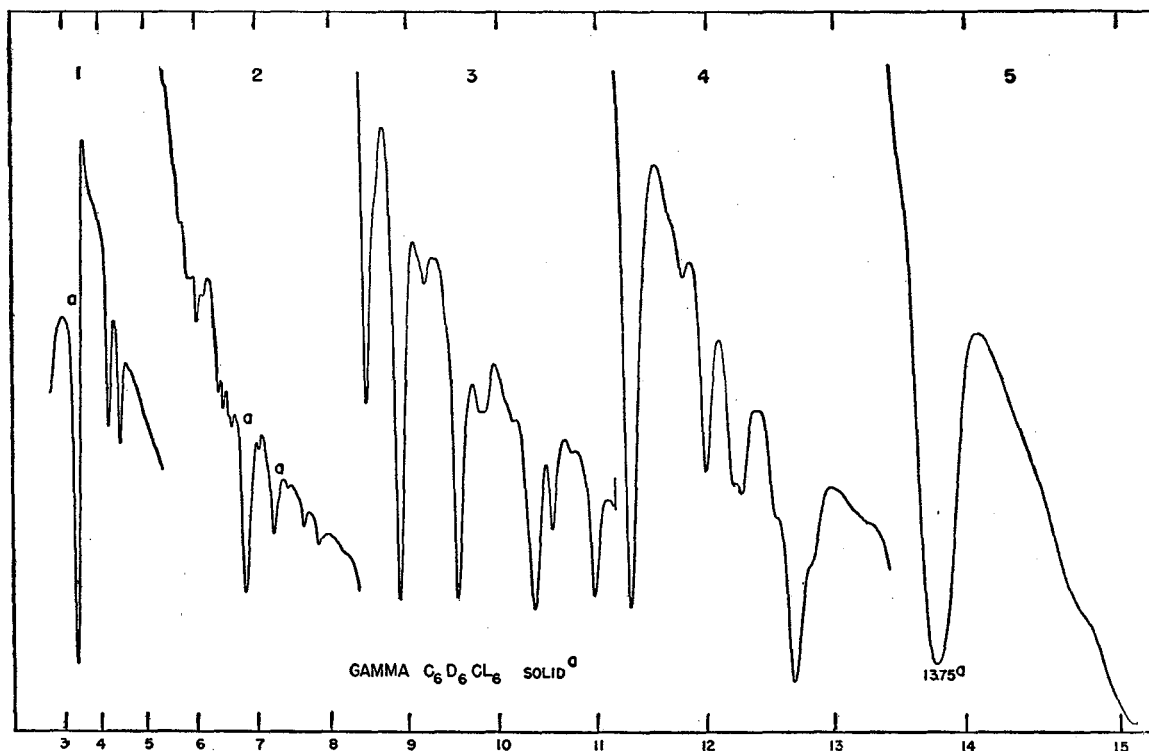

Figure 3.   Infrared Absorption Spectra

a.   Bands due to petrolatum vehicle used in making absorption layers

obtained from the absorption measurement made at the wave length least perturbed in an unfavorable direction by the presence of the impurity.

A careful study of the effect of small amounts (about 1% or less) of the alpha isomer has shown that the most accurate value of $F\gamma$ is obtained through use of the observed $f\gamma P$ value only. This is to be expected in view of the fact that the simple dilution effect which the presence of, say, 1% of the alpha isomer would have at all wave lengths is partially compensated for at the 11.83-mu band by the significant absorption of the alpha isomer due to the overlap of the 11.67-mu alpha and the 11.83-mu gamma bands. There is no equivalent effect at the 13.75-mu deutero gamma isomer band, since the protio alpha isomer has no absorption band at all in this region. Even this method of computation does not give an entirely accurate value for $F\gamma$, as Table IV show.

The average deviation from the known values is about + 0.5 unit and is always positive, indicating that the optical density measured at 11.83 mu is too large, because of the overcompensation of the alpha dilution effect by the alpha absorption effect. The degree of overcompensation, however, is such that the error in the accuracy of the final result obtained in this manner is smaller than that obtained by the other two methods of computation.

Naturally, this somewhat arbitrary treatment can be avoided by sufficient purification of the isolated specimen, so that all three methods of computation would give results of equal accuracy, but the authors have found it impractical, in general, to recrystallize sufficiently to remove the last few tenths per cent of the alpha isomer. Instead they prefer to correct the final result by subtracting 0.5 unit.

The data in Table V illustrate the precision in the determination of the infrared optical density measurements. These measurements were made with a known mixture of the pure deutero and protio gamma isomers.

Thus it appears that the most accurate representation of the assays of this dilution method is expressed by the following:

Table IV. Analytical Results Obtained with Known Mixtures[a]

Known Percentage of Gamma Isomer	Experimental Percentage of Gamma Isomer $F\gamma$[b]	Difference
20.0	21.2	+1.2
20.0	21.1	+1.1
20.0	20.1	+0.1
15.1	15.1	+0.0
12.0	12.7	+0.7
12.0	12.0	+0.0
10.0	10.7	+0.7
20.0	21.1	+1.1
12.0	12.0	+0.0

[a] In every case a mixture of all four common isomers was used containing 60 to 70% of the alpha isomer, 10% of the beta isomer, and 10% of the delta isomer.

[b] $F\gamma$ values calculated using only observed $f\gamma P$ values.

Table V. Reproducibility of Infrared Determination of $f\gamma P$ Value for a Known Mixture Containing 60.2% of Gamma $C_6H_6Cl_6$

Time, Days	$f\gamma P$ at 13.75 Mu	$f\gamma P$ at 11.83 Mu	Average	Difference[a]
1	61	60.5	60.8	+0.8
2	60	60	60.0	−0.2
3	60	61.5	60.8	−0.2
8	60	60.5	60.3	−0.2
9	60	61	60.5	−0.2
Mixture recrystallized from ethylene glycol–water solvent	61	60	60.5	+0.8
			Av.	±0.2

[a] Computed from 13.75 mu $f\gamma P$ values.

$$F\gamma_{true} = (F\gamma_{obsd.} - 0.5) \pm 0.4$$

Table VI presents the results obtained with actual commercial benzene hexachloride crudes. These data also illustrate the degree of precision attainable for the complete analytical procedure when used in assaying typical chlorination crudes. In some of these samples as much as 10 to 15% of oily impurities were known to be present. Moreover, satisfactory assays have been carried out with samples containing as little as about 5% of the gamma isomer.
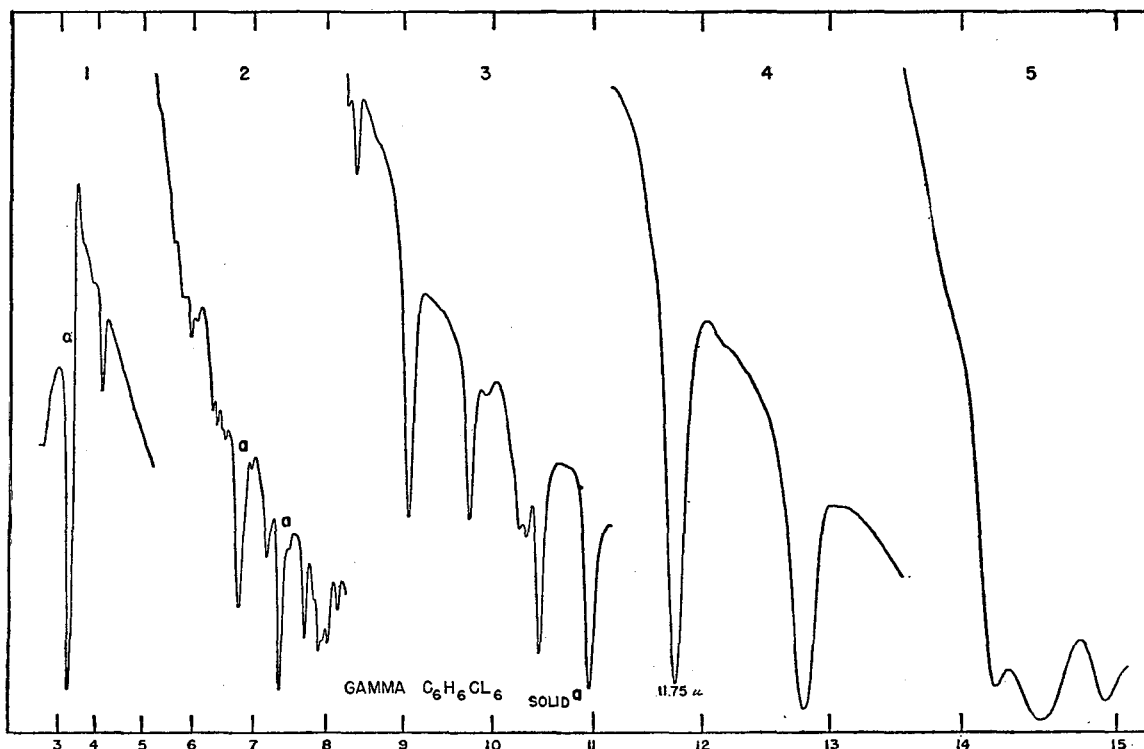

Figure 4. Infrared Absorption Spectra

a. Bands due to petrolatum vehicle used in making absorption layers

Table VI. Analysis of Crude Benzene Hexachlorides

Crude	$F\gamma$
1	12.7, 12.8
2	14.0, 14.5, 13.7
3	17.0, 17.0, 17.6, 16.9
4	11.2, 11.4, 11.8, 11.8, 11.4
5	12.9, 12.9
6	16.2, 16.4, 16.0

SUMMARY

A mass isotope dilution method has been developed for absolute determination of the gamma isomer and, in principle, for some of the other known isomers of benzene hexachloride in crude benzene chlorination products. In particular, the use of infrared spectrophotometry as a means of determining the extent of the mass isotope dilution has been described and its extension as a general absolute assay technique for the analysis of many different kinds of substances under a wide variety of conditions visualized.

In general, it would appear much easier to introduce deuterium into an organic molecule as a marking atom than practically any other kind of atom, the more so if the organic molecule in question cannot be synthesized by other than natural methods, for hydrogen exchange is of far more common occurrence and more easily achieved under sufficiently mild conditions than is true for other kinds of atoms. Because the introduction of deuterium into a molecule results, in general, in rather extensive changes in its infrared spectrum, it should always be possible to determine the extent of the deuterium isotope dilution by such means. Even under the most unfavorable conditions where other changes in the infrared spectrum are only trivial the presence of the C-D linear stretching vibration at about 4.5 mu, a region not generally interfered with by other types of vibrations, would provide a means of analysis. Moreover, for compounds whose solubility properties preclude the use of any otherwise usable solvent, one can use solids equally effectively (1, 13). Thus the combined general methods employed in this paper are of considerable scope and interest from the point of view of the absolute analysis of organic substances occurring in complex media. The use of the concept of isotope dilution in analysis is not new (15), but the specific use of infrared spectrophotometry in determining the mass isotope dilution in place of the older and more cumbersome combustion–density of water methods is believed to be substantially original (14).

Because impurities are without effect upon the accuracy of this method, its reliability is limited only by its precision, which is constant over practically the whole range of concentrations, and moreover, as the precision would appear necessarily superior to that attainable by direct infrared analysis, the isotope dilution method must take precedence over it and all other methods as a primary assay by which the reliability of other methods may be gaged.

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A Flowmeter for High Temperature Gases

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THE development and specification of pyrotechnic fuel mixtures during World War II gave rise to the need for a simple but fairly accurate method of measuring the instantaneous volume rate of gas evolved (2). The required apparatus consists essentially of a sharp-edged orifice fitted with a shielded thermocouple in a high velocity gas stream to permit the simultaneous measurement of hot gas temperature and pressure across the orifice. A baffle was provided to prevent the thermocouple from "seeing" the incandescent surface of the pyrotechnic mixture. This device came to be known as a volume tester.

APPARATUS

The device was constructed in several sizes. Figure 1 shows a cross section through a typical unit.

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The gas from the surface of the pyrotechnic mixture flows around the baffle plate and through the tube containing the thermocouple. This tube serves the dual purpose of imparting a relatively high velocity to the gas flowing by the thermocouple and of shielding the latter from the cooler sides of the apparatus. The gases then exhaust through the orifice to the atmosphere. A pressure connection is provided in the side of the unit near the orifice, which is connected to a manometer or pressure gage. Chromel-alumel B. and S. gage 22 thermocouple wires were found satisfactory with gas temperatures approaching 2000° F. All except the junction was coated with Sauereisen for protection. The calibration of the couple was checked at a known temperature after each one to three tests.

The fuel is ignited and temperature and pressure readings are taken at frequent intervals throughout the burning time.

CALCULATIONS

The relationship between pressure drop across the orifice and the weight rate of flow is given by the Equation (1, 3)

A method of measuring the flow of hot gases from a pyrotechnic fuel mixture is
described. The gases pass over a shielded thermocouple and are then exhausted
through a sharp-edged orifice. The flow rate is corrected for gradual changes
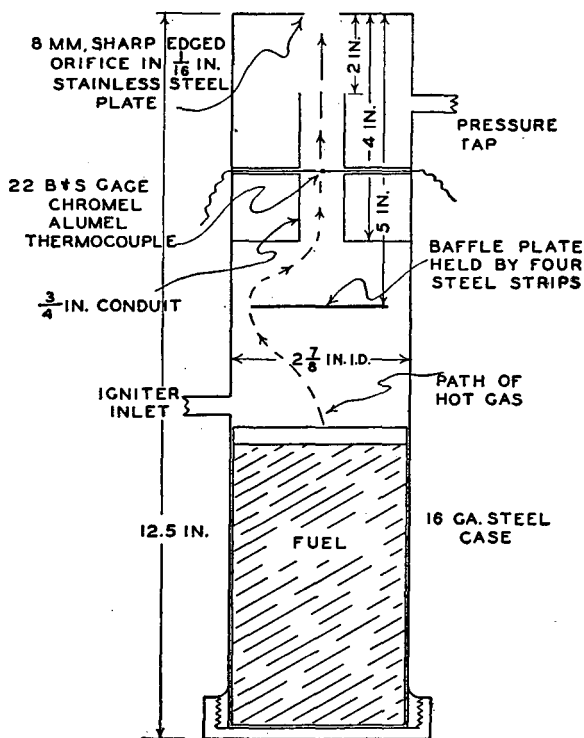in gas temperature and pressure. The device is termed a volume tester.

Figure 1. Volume Tester for Measuring Instantane-
ous Hot Gas Flow Rates

$$W = cyS_0 \sqrt{\frac{2g_c\rho_1\,(p_1 - p_2)}{(1 - B^4)}} \qquad (1)$$

where

$$y = 1 - \frac{p_1 - p_2}{p_1 k}\,[0.41 + 0.35\,B^4]$$

Equation 1 is accurate within 1% for p_2/p_1 not less than 0.8
and the error is not serious when p_2/p_1 approaches 0.5. For a
given unit and gas $\dfrac{0.41 + 0.35\,B^4}{k} = K$, a constant. The in-
stantaneous volumetric rate of flow in terms of volume reduced
to standard conditions (60° F. and 1 atmosphere in this paper)
is given by

$$q_s = W/\rho_s$$

Then $\quad q_s = \left[cS_0\,\sqrt{\dfrac{2g_c}{(1 - B^4)}}\right]y\,\sqrt{\Delta p\,\dfrac{\rho_1}{\rho_s^2}} = c'y\,\sqrt{\dfrac{\Delta p\,\rho_1}{\rho_s^2}} \qquad (2)$

The perfect gas law may be used.

$$\frac{\rho_1}{\rho_s} = \frac{520\,p_1}{14.7 \times 144 \times T_1}$$

$$\rho_s = \frac{M}{379}$$

$$q_s = c''y\,\sqrt{\frac{p_1\Delta p}{MT_1}} \qquad (3)$$

When the burning rate is not constant and causes variations
in the flow of gas during the test, a plot of q_s against time may be
integrated graphically to give the total volume of gases generated,
reduced to standard conditions. From the equation

$$W = q_s\rho_s = q_s\,\frac{M}{379}$$

the total weight of gas is determined and compared with the
weight of the pyrotechic mixture to obtain a material balance.
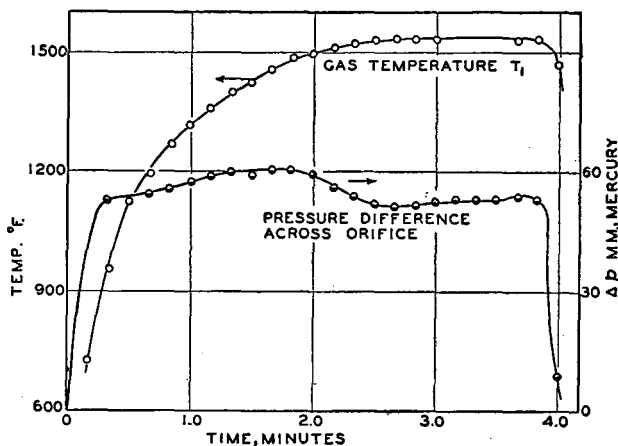
Figure 2. Relation of Gas Temperature and Pressure
Difference across Orifice to Time

Similarly the instantaneous volumetric rate in terms of actual
volume at the temperature and pressure in the unit is given by
the equation·

$$q_1 = W/\rho_1$$

$$q_1 = c'y\,\sqrt{\frac{\Delta p}{\rho_1}} = c'''y\,\sqrt{\frac{T_1\Delta p}{Mp_1}} \qquad (4)$$

For two gases of different average molecular weight, M_a and
M_b, but with the same value of k, each flowing through the ori-
fice under identical conditions of temperature and pressure, the
ratio of their volume flow rates (either actual or reduced to
standard conditions) is

$$\frac{q_a}{q_b} = \sqrt{\frac{M_b}{M_a}} \qquad (5)$$

This makes it possible to calculate the rates of flow on the basis of an assumed molecular weight and later to correct these when the true molecular weight is determined by gas analysis.

From equation 2

$$q_s = c'y \sqrt{\frac{\Delta p \, \rho_1}{\rho_s \, \rho_s}} = C \, y \, \sqrt{\Delta p} \, \sqrt{\frac{\rho_1}{\rho_s}} \qquad (6)$$

and from Equation 4

$$q_1 = c'y \sqrt{\frac{\Delta p \, \rho_s}{\rho_1 \, \rho_s}} = C \, y \, \frac{\sqrt{\Delta p}}{\sqrt{\frac{\rho_1}{\rho_s}}} \qquad (7)$$
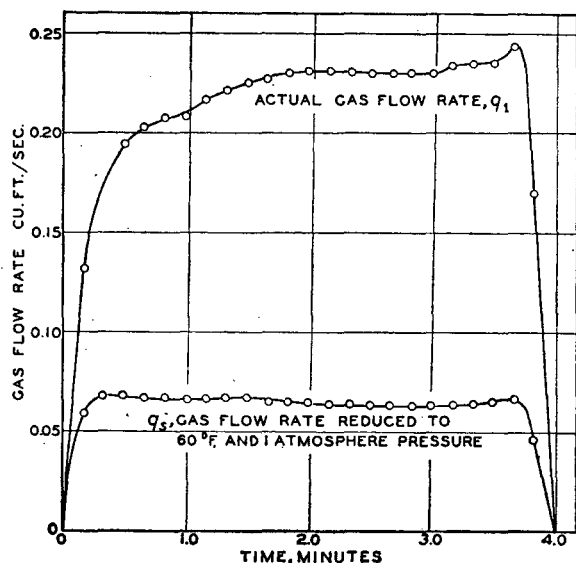

Figure 3. Relation of Gas Flow Rates to Time

Gas volumes measured under actual conditions of temperature and pressure and also at 60° F. and 1 atmosphere

The steps in making the calculations may be summarized as follows:

1. Temperatures and pressures (Δp) are tabulated for a number of time intervals.
2. The values of p_1 (barometric pressure $+\Delta p$) are calculated.
3. The values of $\frac{\rho_1}{\rho_s} \left(= \frac{p_1 T_s}{p_s T_1} \right)$ and y are determined.
4. The instantaneous values of q_s and q_1 based on average values of molecular weight and k are obtained from Equations 6 and 7.
5. The flow rates, q_s, are then plotted against time and integrated graphically to obtain the total volume of gas (corrected to standard conditions) emitted during the test period.
6. This value is corrected for molecular weight when necessary, converted to total mass, and used in a material balance as a check on the validity of the measured flow rates.

The method has consistently given material balances which check within ±5%. It is felt that this is reasonable accuracy in view of the high temperatures and varying flow rates encountered.

Typical curves of pressure and temperatue versus time and the calculated curves of actual volume rate and volume rate corrected to standard conditions are shown in Figures 2 and 3.

When used as a standard test procedure the calculations may be simplified by preparing suitable graphs and a nomograph. In step 3 a nomograph is useful for calculating ρ_1/ρ_s from the measured values of p_1 and T_1. In step 4 a series of lines at constant ρ_1/ρ_s of either q_1 or q_s as ordinate against Δp as abscissa on log-log paper may be prepared for constant barometric pressure

and k. These lines may be constructed for a reference gas, such as air. The values of q_s read from these curves may be integrated over the period of time covered by the test and the total gas volume obtained in terms of this reference gas. Equation 5 will then serve to convert the integrated flow of reference gas to the flow of actual test gas.

The application of continuously recording temperature and pressure difference instruments to the procedure will be self-evident. The method may also be applied to other orifice installations for measuring gas flow.

ACKNOWLEDGMENT

This paper is based on work done at the Munitions Development Laboratory at the University of Illinois during World War II. E. D. Shippee contributed to the project.

NOMENCLATURE

$B = \dfrac{D_0}{D_1}$

c = orifice constant; a value of 0.61 was used

$c' = c \, S_0 \sqrt{\dfrac{2g_e}{(1 - B^4)}}$

$c'' = c' \sqrt{\dfrac{520 \times 379}{14.7 \times 144}} = 9.64 \, c'$

$c''' = c' \sqrt{\dfrac{379 \times 14.7 \times 144}{520}} = 39.3 \, c'$

$C = \dfrac{c'}{\sqrt{\rho_s}} = \dfrac{19.4 c'}{M}$

D_0 = orifice diameter, feet
D_1 = diameter upstream from the orifice, feet

$g_e = 32.17 \dfrac{\text{lb. (mass)} \times \text{feet}}{\text{lb. (force)} \times \text{sec.}^2}$

$K = \dfrac{0.41 + 0.35 B^4}{k}$, a constant for a given unit and gas

$k = \dfrac{c_p}{c_v}$, ratio of specific heat at constant pressure to specific heat at constant volume

M = molecular weight of gas
p_1 = absolute pressure upstream from the orifice, pounds (force) per square foot
$\Delta p = p_1 - p_2$, difference in pressure across orifice
q_1 = volumetric rate of flow measured at the temperature and pressure upstream from the orifice, cubic feet per second
q_s = volumetric rate of flow measured at 60° F. and 14.7 pounds per square inch absolute pressure
S_0 = cross-sectional area of orifice, square feet
T_1 = absolute temperature upstream from orifice, degrees Rankine
W = mass rate of flow, pounds (mass) per second
y = correction factor, $1 - \dfrac{p_1 - p_2}{p_1 k}(0.41 + 0.35 B^4)$
ρ_1 = gas density, upstream from orifice, pounds per cubic foot
ρ_s = gas density at 60° F. and 14.7 pounds per square inch absolute, pounds per cubic foot

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Determination of Zirconium by Precipitation from Homogeneous Solution

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Zirconium can be precipitated quantitatively from solutions 3.6 N in hydrochloric or sulfuric acid by adding 15 to 20 ml. of trimethyl phosphate and heating for 12 to 15 hours. The precipitate obtained is a mixture of zirconyl methyl phosphate, ZrO-[H(CH$_3$)(PO$_4$)]$_2$.2H$_2$O, and zirconyl phosphate, ZrO-(H$_2$PO$_4$)$_2$. Upon ignition at 900° to 950° C. this precipitate is completely converted to zirconium pyrophosphate, which is weighed. The method can be used to determine zirconium in samples containing from 2 to 60 mg. of zirconium oxide. Antimony, bismuth, cerous, and stannic ions interfere. Large amounts of ferric, titanium, thorium, and uranyl ions give high results. When acid solutions containing zirconyl ions are treated with an excess of meta-

phosphoric acid, a soluble metaphosphate complex is formed. A precipitate of zirconyl phosphate is slowly deposited at room temperature. The precipitate thus obtained is more dense than the precipitate formed by direct addition of a soluble orthophosphate, although not so dense as that obtained by precipitation with trimethyl phosphate. This precipitate does not decrepitate upon ignition and is completely converted to zirconium pyrophosphate by heating at 900° to 950° C. Metaphosphoric acid can be used to determine zirconium in samples containing from 0.2 to 200 mg. of zirconium oxide. Best results were obtained by adding a large excess of metaphosphoric acid to solutions 3.6 N in sulfuric acid. Bismuth, stannic, and perchlorate ions interfered.

ONE of the most widely used methods for the determination of zirconium consists of precipitating the zirconium as zirconyl phosphate, ZrO(H$_2$PO$_4$)$_2$, from a warm 3.6 N sulfuric acid solution by addition of a large excess of ammonium phosphate. After filtering and washing with a 5% solution of ammonium nitrate, the precipitate is ignited to the pyrophosphate, ZrP$_2$O$_7$, and weighed (*2–4*).

The method can be used accurately only for the determination of small amounts of zirconium (up to 20 mg. of zirconium oxide). The precipitate of zirconyl phosphate is bulky and gelatinous, and therefore difficult to filter and wash. Upon ignition the precipitate decrepitates and losses may occur.

Many normally gelatinous precipitates can be improved by slowly forming the precipitating ion in homogeneous solution by hydrolysis. Willard and Freund (*6*) used triethyl phosphate to fractionate zirconium and hafnium by precipitation as the phosphates. They found that acid solutions containing zirconyl ions gave a dense crystalline precipitate of zirconyl ethyl phosphate, ZrO[H(C$_2$H$_5$)(PO$_4$)]$_2$.2H$_2$O, when heated with triethyl phosphate. This method gave a more efficient fractionation than the usual methods in which the orthophosphate ion was added directly to the solution (*6*). No attempts were made by the authors, however, to use this reagent for the separation and quantitative determination of zirconium in the presence of other elements.

PRECIPITATION AND DETERMINATION OF ZIRCONIUM BY HYDROLYSIS OF ORGANIC PHOSPHATES

In this investigation of the quantitative precipitation of zirconium by hydrolysis of organic phosphates, three reagents were studied: triethyl phosphate, trimethyl phosphate, and tetraethyl pyrophosphate. All these substances are completely miscible with water and dilute mineral acids. When added to a solution containing zirconyl ions, no precipitates resulted unless the solutions were heated for a time.

Experimental. Standard solutions were prepared by dissolving chemically pure zirconium sulfate and zirconium nitrate in 1 N sulfuric acid, taking 25-ml. portions with a pipet, and determining the zirconium content by precipitation with cupferron following the procedure given by Hillebrand and Lundell (*1*). The same pipet was used to measure the samples used for the experimental work.

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Preliminary experiments showed that dense, crystalline precipitates resulted when 3.6 N sulfuric acid solutions containing zirconyl ions were heated with triethyl phosphate, trimethyl phosphate, and tetraethyl pyrophosphate. After the corresponding precipitate was filtered off and the filtrate made alkaline with ammonium hydroxide, no precipitate of zirconium hydroxide resulted; the zirconium was quantitatively precipitated by the hydrolysis of the organic phosphates.

Quantitative precipitation could be achieved with triethyl phosphate only upon heating for 18 to 24 hours at the boiling point, whereas trimethyl phosphate and tetraethyl pyrophosphate gave quantitative precipitation upon heating for 12 to 15 hours. As triethyl phosphate had no advantages over the other reagents, no further studies were made with it.

Further investigation of tetraethyl pyrophosphate showed that this reagent also formed a precipitate when heated with ferric ions. As iron is usually associated with zirconium in its ores and alloys, no further investigations were made with this reagent and full attention was given to trimethyl phosphate.

Trimethyl Phosphate as Reagent. As the precipitate obtained by the hydrolysis of triethyl phosphate was shown to have the formula ZrOH(C$_2$H$_5$)(PO$_4$)$_2$.2H$_2$O (*6*), the precipitate obtained with triethyl phosphate was expected to be ZrO[H(CH$_3$)(PO$_4$)]$_2$.-2H$_2$O. The precipitate, however, was found to be variable in composition and x-ray diffraction studies showed that it also contained varying amounts of zirconyl phosphate. Hence, accurate results could not be obtained by weighing the precipitate directly. Upon ignition at 950° C. for 2 hours, the precipitate was converted completely to zirconium pyrophosphate, ZrP$_2$O$_7$. X-ray diffraction pictures showed that this ignited precipitate was of the same composition as that obtained by ignition of pure zirconyl phosphate.

To study the effect of different acids of various concentrations, the following procedure was used:

Procedure. The volume of the solution was adjusted to 150 to 200 ml. and the acidity adjusted to the desired concentration. Fifteen to 20 ml. of trimethyl phosphate were then added and the sample was heated just under its boiling point for at least 12 hours. Longer periods of heating are not harmful. Water was added occasionally to replace that lost by evaporation. After heating for a sufficient length of time, the solutions were allowed to cool, then filtered through No. 40 Whatman filter paper and washed with 250 to 300 ml. of cold 5% ammonium nitrate solution. The beaker was wiped out with a small piece of filter paper

to remove any zirconyl phosphate which still adhered to the sides of the beaker

The precipitate was ignited over a Meker burner until the filter paper had completely charred, then in a muffle at 900° to 950° C. to constant weight. The theoretical factor, $ZrO_2/ZrP_2O_7 = 0.4657$, was used to compute the weight of zirconium oxide (Table I). All results given in this paper are averages of two closely agreeing determinations.

These data show that trimethyl phosphate can be used to precipitate zirconium quantitatively from 3.6 N solutions of hydrochloric, nitric, or sulfuric acid. If the solutions are filtered hot or if the acid concentrations are more than 3.6 N, the results will be low, owing to the increased solubility of the precipitate. Sulfuric and hydrochloric acid solutions of the above concentration must be heated for at least 12 hours to ensure complete precipitation, and more dilute solutions must be heated much longer. Nitric acid solutions must be heated for at least 24 hours. Perchloric acid gives low results probably due to the coprecipitation of some perchlorate.

Trimethyl phosphate was used to precipitate various amounts of zirconium from 3.6 N hydrochloric and sulfuric acid solutions to determine the useful range of the method (Table II). The procedure followed was the same as in the previous experiment.

Tables I and II show that trimethyl phosphate can be used as a reagent to determine zirconium in samples containing from 2 to 60 mg. of zirconium oxide. Larger amounts give low results, probably caused by partial hydrolysis of the precipitate.

Table I. Determination of Zirconium in Pure Solution

Acid and Normality	Hours Heated	Weight of ZrP₂O₇, Gram	ZrO₂ Calcd., Gram	ZrO₂ Taken, Gram	Error, Gram
3.6 N H₂SO₄	8	0.1251	0.0581	0.0602	-0.0021ᵃ
3.6 N H₂SO₄	12	0.1209	0.0562	0.0562	0.0000
7.0 N H₂SO₄	12	0.1290	0.0599	0.0602	-0.0003
3.6 N HNO₃	24	0.1296	0.0602	0.0602	0.0000
3.6 N HCl	12	0.1212	0.0563	0.0562	+0.0001
7.0 N HCl	12	0.1288	0.0598	0.0602	-0.0004
3.6 N HClO₄	12	0.1234	0.0573	0.0602	-0.0029
3.6 N H₂SO₄	12	0.1262	0.0586	0.0602	-0.0016ᵇ

ᵃ Zr detected in filtrate.
ᵇ Filtered hot.

Table II. Determination of Range of Method

Acid	Total Vol. of Soln., Ml.	(CH₃)₃PO₄ Added, Ml.	Weight of ZrP₂O₇, Gram	ZrO₂ Calcd., Gram	ZrO₂ Taken, Gram	Error, Gram
H₂SO₄	50	5	0.0048	0.0022	0.0022	0.0000
HCl	50	5	0.0047	0.0022	0.0022	0.0000
H₂SO₄	100	10	0.0098	0.0046	0.0045	+0.0001
HCl	100	10	0.0097	0.0045	0.0045	0.0000
H₂SO₄	100	10	0.0240	0.0112	0.0112	0.0000
HCl	100	10	0.0238	0.0111	0.0112	-0.0001
H₂SO₄	100	10	0.0480	0.0223	0.0225	-0.0002
HCl	100	10	0.0478	0.0222	0.0225	-0.0003
H₂SO₄	150	30	0.2400	0.1115	0.1124	-0.0009
HCl	150	30	0.2395	0.1113	0.1124	-0.0011
H₂SO₄	175	35	0.3578	0.1663	0.1686	-0.0023
HCl	175	35	0.3574	0.1661	0.1686	-0.0025
H₂SO₄	200	45	0.4800	0.2230	0.2248	-0.0018
HCl	200	45	0.4770	0.2217	0.2248	-0.0031

Table III. Interferences

Added Substance, Gram	Separations in 3.6 N H₂SO₄ ZrO₂ calcd., gram	ZrO₂ taken, gram	Error, gram	Separations in 3.6 N HCl ZrO₂ calcd., gram	ZrO₂ taken, gram	Error, gram
0.25 Sb⁺⁺⁺ᵃ	0.0622	0.0602	+0.0020	0.0624	0.0602	+0.0022
0.25 Bi⁺⁺⁺ᵃ	0.0674	0.0602	+0.0072	0.0623	0.0602	+0.0021
0.20 Ce⁺⁺⁺	0.0587	0.0562	+0.0025	0.0604	0.0562	+0.0042
0.25 Sn⁺⁺⁺⁺ᵃ	0.0725	0.0602	+0.0123	0.0660	0.0602	+0.0058
0.25 UO₂⁺⁺	0.0610	0.0602	+0.0008	0.0609	0.0602	+0.0007
0.25 Fe⁺⁺⁺	0.0602	0.0562	+0.0040	0.0598	0.0562	+0.0036
0.05 Fe⁺⁺⁺	0.0569	0.0562	+0.0007	0.0567	0.0562	+0.0005
0.025 Fe⁺⁺⁺	0.0563	0.0562	+0.0001	0.0562	0.0562	0.0000
0.050 Th⁺⁺⁺⁺	0.0706	0.0562	+0.0144	0.0722	0.0562	+0.0160
0.010 Th⁺⁺⁺⁺	0.0568	0.0562	+0.0006	0.0567	0.0562	+0.0005
0.005 Th⁺⁺⁺⁺	0.0563	0.0562	+0.0001	0.0563	0.0562	+0.0001
0.100 TiO₂ᵇ	0.0577	0.0562	+0.0015	..	..	....
0.025 TiO₂ᵇ	0.0572	0.0562	+0.0010	...	..	....
0.010 TiO₂ᵇ	0.0563	0.0562	+0.0001	..	..	....

ᵃ 10 g. of tartaric acid added to H₂SO₄ solution.
ᵇ 5 ml. of 30% H₂O₂ added every 2 hours.

Table IV. Determination of Zirconium in Pure Solutions

Acid and Normality	Weight of ZrP₂O₇, Gram	ZrO₂ Calcd., Gram	ZrO₂ Taken, Gram	Error, Gram
1.8 N H₂SO₄	0.1194	0.0555	0.0562	-0.0007
3.6 N H₂SO₄	0.1213	0.0564	0.0562	+0.0002
7.2 N H₂SO₄	0.1194	0.0555	0.0562	-0.0007
3.6 N HCl	0.0921	0.0428	0.0433	-0.0005
3.6 N HNO₃	0.1299	0.0604	0.0602	+0.0002
3.6 N HClO₄	0.1274	0.0592	0.0602	-0.0010
3.6 N H₂SO₄	0.0916	0.0426	0.0433	-0.0007ᵃ

ᵃ Filtered hot.

Separations. To determine the influence of other ions, precipitations were made both in 3.6 N sulfuric acid and in 3.6 N hydrochloric acid using the procedure described. Successful determinations were made in the presence of aluminum, arsenate, borate, cadmium, calcium, chromic, cobalt, cupric, magnesium, manganese, mercuric, nickel, potassium, sodium, tartrate, vanadyl, and zinc ions. When more than 0.025 gram of ferric or 0.010 gram of thorium ions were present, high results were obtained. The presence of uranium also caused slightly high results. Antimony, bismuth, cerous, and stannic ions interfered. The extent of these interferences is given in Table III.

DETERMINATION OF ZIRCONIUM BY HYDROLYSIS OF META- PHOSPHORIC ACID

In studying the reaction of metaphosphoric acid with the zirconyl ion, it was found that a soluble metaphosphate complex was formed with the zirconyl ion in acid solutions. When these solutions were allowed to stand at room temperature, a granular precipitate of zirconyl phosphate was thrown down. X-ray diffraction pictures of this precipitate showed it to be identical with the precipitate obtained by adding a soluble orthophosphate to acid solutions of the zirconyl ion. Although the precipitate obtained with metaphosphoric acid was not so dense and crystalline as those obtained by the hydrolysis of organic phosphates, it was much better than that obtained by direct precipitation with the orthophosphate ion. Further experiments showed that the zirconium was quantitatively precipitated if a large excess of metaphosphoric acid was added.

Experimental. To determine the conditions necessary for quantitative precipitation of zirconium, precipitations were made in the presence of different acids of various concentrations. The following procedure was used in the absence of other metals:

Five grams of reagent quality metaphosphoric acid dissolved in 25 ml. of water were added to 150 to 175 ml. of an acid solution containing a known quantity of zirconyl ions. This solution was allowed to stand 12 hours at room temperature. During this time a precipitate of zirconyl phosphate was slowly formed. The solution was then heated to boiling and maintained just under its boiling temperature for 1 hour to ensure complete hydrolysis of the metaphosphoric acid. After cooling, the solution was filtered and the precipitate washed with cold 5% ammonium nitrate solution and finally ignited at 900° to 950° C. in a muffle. The factor $ZrO_2/ZrP_2O_7 = 0.4657$ was used to compute the weight of zirconium oxide from the weight of pyrophosphate (Table IV).

Quantitative results were obtained in the 3.6 N nitric and sulfuric acid solutions. Perchloric acid gave low results, as it did in precipitation by the hydrolysis of organic phosphates. The determinations made in the hydrochloric acid were slightly low. The precipitates from the sulfuric acid were the most dense; therefore, this acid was used in the following experiments to determine the range of the method. Varying amounts of zirconyl sulfate were added to 3.6 N sulfuric acid solutions and the zirconium was determined by the procedure described above (Table V).

Tables IV and V show that metaphosphoric acid can be used as a reagent to determine 0.2 to 200 mg. of zirconium oxide. For amounts less than 10 mg. of zirconium oxide, the method had no particular ad-

Table V. Determination of Range of Method

Total Vol. of Solution, Ml.	HPO₃ Added, Gram	ZrP₂O₇, Gram	ZrO₂ Calcd., Gram	ZrO₂ Taken, Gram	Error, Gram
50	2	0.0004	0.0002	0.0002	0.0000
50	2	0.0018	0.0008	0.0011	−0.0003
50	2	0.0041	0.0019	0.0017	+0.0002
50	2	0.0183	0.0085	0.0086	−0.0001
100	5	0.0372	0.0174	0.0173	+0.0001
200	5	0.2190	0.1017	0.1016	+0.0001
200	5	0.2592	0.1204	0.1204	0.0000
200	5	0.3290	0.1529	0.1524	+0.0004
200	5	0.4381	0.2036	0.2032	+0.0004

Table VI. Interferences

Added Substance, Gram	ZrO₂ Calcd., Gram	ZrO₂ Taken, Gram	Error, Gram
0.10 Ce⁺⁺⁺	0.0640	0.0508	+0.0132
0.10 Th⁺⁺⁺⁺	0.0558	0.0508	+0.0050
0.025 Th⁺⁺⁺⁺	0.0651	0.0602	+0.0049
0.010 Th⁺⁺⁺⁺	0.0510	0.0508	+0.0002
0.005 Th⁺⁺⁺⁺	0.0508	0.0508	0.0000
0.10 TiO₂	0.0985	0.0508	+0.0473
0.10 TiO₂ + 5 ml 30% H₂O₂	0.0517	0.0508	+0.0009
0.050 TiO₂ + H₂O₂	0.0513	0.0508	+0.0005
0.020 TiO₂ + H₂O₂	0.0511	0.0508	+0.0003
0.010 TiO₂ + H₂O₂	0.0509	0.0508	+0.0001
0.10 UO₂⁺⁺	0.0514	0.0508	+0.0006
0.25 Fe⁺⁺⁺	0.0541	0.0508	+0.0033
0.10 Fe⁺⁺⁺	0.0596	0.0602	−0.0006
0.050 Fe⁺⁺⁺	0.0598	0.0602	−0.0004
0.025 Fe⁺⁺⁺	0.0600	0.0602	−0.0002
0.010 Fe⁺⁺⁺	0.0600	0.0602	−0.0002
0.20 Bi⁺⁺⁺ + H₂C₄H₄O₆	0.1329	0.0562	+0.0767
0.20 Sn⁺⁺⁺⁺ + H₂C₄H₄O₆	0.1399	0.0562	+0.0837
0.25 TiO₂ + 5 ml. H₂O₂	0.0600	0.0602	−0.0002
0.10 Th⁺⁺⁺⁺	0.0523	0.0508	+0.0015
0.050 Th⁺⁺⁺⁺	0.0600	0.0602	−0.0002
1.0 Fe⁺⁺⁺	0.0600	0.0602	−0.0002

vantage over direct precipitation with ammonium phosphate. In either case the precipitate is small and can be easily filtered and washed. The method is not recommended for amounts more than 200 mg. of zirconium oxide. With larger amounts the bulk of the precipitate would make its manipulation difficult.

To investigate the separation from other metals, precipitations were made from 200 ml. of 3.6 N sulfuric acid using the procedure described. Successful separations were made from aluminum, arsenate, borate, cadmium, chromic, cerous, cobalt, cupric, magnesium, manganous, mercuric, nickel, potassium, sodium, tartrate, vanadyl, yttrium, and zinc ions. The presence of more than 0.025 gram of ferric ions, 0.010 gram of thorium, or 0.020 gram of titanium oxide interfered. Bismuth, stannic, and perchlorate ions interfered. The extent of the interferences is shown in Table VI.

Successful determinations were made in the presence of 0.25 gram of titanium dioxide and 0.050 gram of thorium by using a double precipitation. Large amounts of iron can be removed by ether extraction and the zirconium then determined in the remaining solution. Determination can also be made in the presence of antimony if tartaric acid is added to prevent hydrolysis.

Procedure. Ore samples were put in solution by fusion with borax and treatment with acids (5). Alloy samples were dissolved in hydrochloric, nitric, or sulfuric acid. The solution was evaporated with sulfuric acid to remove the excess of the other acids. If barium, lead, or large amounts of calcium were present, they were removed by precipitation with sulfuric acid. The total volume of the solution was adjusted to 150 to 200 ml. and made 3.6 N in sulfuric acid (10% by volume of concentrated sulfuric acid). This solution was cooled and 5 grams of metaphosphoric acid dissolved in 25 ml. of water were added to it. If titanium was present, 5 ml. of 30% hydrogen peroxide were also added. This solution was allowed to stand at room temperature for about 12 hours, at the end of which time a granular precipitate of zirconyl phosphate had settled out. The solution was then heated just under its boiling point and held at this temperature for 1 hour. If iron was present, the heating was continued for an extra hour to ensure complete solution of any precipitated ferric metaphosphate. The sample was allowed to cool to room temperature, then filtered through Whatman No. 40 filter paper, and washed with about 300 to 500 ml. of 5% ammonium nitrate solution also at room temperature. The beaker was

wiped out with a small piece of filter paper to remove any zirconyl phosphate which adhered to the walls of the beaker.

The filter paper and the precipitate were slowly charred, then ignited to constant weight at 900° to 950° C. in a muffle. The precipitate of zirconium pyrophosphate should be pure white. The theoretical factor ZrO₂/ZrP₂O₇ = 0.4657 was used to compute the weight of zirconium oxide.

If antimony was present, 10 grams of tartaric acid were added to the sulfuric acid solution to prevent hydrolysis of the antimony ion.

Zirconium can be determined in the presence of antimony and bismuth if the precipitation is made from 3.0 N hydrochloric acid solution instead of sulfuric acid. In this case the precipitate must be washed first with 200 ml. of 5% hydrochloric acid solution which also contains 2% of ammonium phosphate, then with 100 ml. of 5% ammonium nitrate solution.

If more than 25 mg. of iron are present, most of it should be removed by extraction with ether. The zirconium determination is then carried out as directed above.

The method will give good separations from as much as 0.250 gram of titanium oxide or 0.050 gram of thorium if a double precipitation is made. The first precipitation should be carried out in the usual manner, and the precipitate filtered and washed with ammonium nitrate. The filter paper and the precipitate are then put back into the original beaker, and 20 ml. of concentrated nitric acid, then 20 ml. of concentrated sulfuric acid are added. The beaker should be covered with a watch glass and heated gently until all the filter paper is destroyed. The watch glass is then elevated and the solution evaporated to fumes of sulfur trioxide. The zirconyl phosphate dissolves in the concentrated sulfuric acid. This solution is cooled and diluted to 200 ml. with water, and 5 ml. of 30% hydrogen peroxide, then 5 grams of metaphosphoric acid dissolved in 25 ml. of water are added. The precipitation, filtration, etc., are carried out as previously directed.

ANALYSIS OF A ZIRKITE ORE

The method was checked by determining the zirconium in a zirkite ore, shown by a qualitative analysis to be composed largely of zirconium oxide. Silica, ferric oxide, titanium oxide, and a trace of vanadium were also present. Thorium, aluminum, and the rare earths were not present in detectable amounts.

For quantiative analysis, the ore was put into solution by fusion with borax. After removal of the silica, the zirconium was determined by the standard cupferron method (5). The zirconium was also determined with metaphosphoric acid using the procedure given.

Table VII. Analysis of Zirkite Ore

Sample	Cupferron		Metaphosphoric Acid	
	Sample, Mg.	ZrO₂, %	Sample, Mg.	ZrO₂, %
1	0.2000	74.51	0.1000	74.35
2	0.2000	74.20	0.1000	74.53
3	0.4000	74.38	0.2000	74.25
Av.		74.36		74.38

The determinations made with the metaphosphoric acid are in close agreement with those of the standard cupferron method. The metaphosphoric acid method is more rapid and requires fewer separations and manipulations. It is, therefore, recommended for the determination of zirconium in ores that contain small amounts of iron, titanium, and thorium.

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Determination of Small Quantities of Oxygen in Hydrocarbon Gases

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A method is described for determining oxygen in gases in very low concentrations up to 2.5%. A known volume of gas is passed repeatedly over copper wire which is moistened with ammoniacal ammonium chloride solution. The amount of dissolved copper is determined by measuring, with a photelometer, the intensity of the blue color in the solution. Saturated or unsaturated hydrocarbon gases do not interfere, but hydrogen sulfide and mercaptans must be removed. The principle is well known; however, a portable apparatus and simple procedure have been developed which minimize the sources of error.

IN THE production of butadiene by cracking of petroleum fractions, oxygen in the cracking gas or finished butadiene is an undesirable contaminant, because it catalyzes the formation of gummy polymers and produces organic peroxides which in certain operations might present a hazard because of their unstable nature.

A sensitive, simple, and rapid method was needed for the determination of oxygen, which would not be subject to interferences from olefinic hydrocarbon gases. An apparatus was desired which would be portable and could be taken to the gas source, thus eliminating the possibility of contamination that exists when a gas sample is taken in a container and transported to the laboratory.

The manganous hydroxide method for determining small amounts of oxygen given by Phillips (2), which is a modification of the Winkler (4) method, and the methods for determining oxygen in gases by the reaction of the oxygen with reduced copper in the presence of ammonia–ammonium chloride as described by MacHattie and Maconachie (1) and Uhrig, Roberts, and Levin (3) were investigated.

The latter method offered the desired sensitivity and freedom from interferences but the apparatus required was complex and nonportable. The design of a simple, portable apparatus which would make possible the use of this method was successfully undertaken.

REAGENTS

Ammonium Hydroxide–Ammonium Chloride Solution. Mix 300 grams of C.P. ammonium chloride, 1000 ml. of C.P. ammonium hydroxide, and 1000 ml. of freshly boiled distilled water, and filter the solution to remove undissolved solids. Keep this solution in a bottle provided with a delivery tube under an atmosphere of essentially oxygen-free gas which can be introduced into the bottle under pressure to force the solution from the bottle when needed.

Standard Copper Solution. Dissolve 3.928 grams of cupric sulfate pentahydrate in exactly 1000 ml. of the ammonium chloride–ammonium hydroxide reagent. One milliliter of solution contains 1 mg. of copper.

Silver Nitrate Solution. Dissolve 20 grams of silver nitrate in 1 liter of water. This solution is used to scrub the gas if it contains hydrogen sulfide or mercaptans (thiols).

APPARATUS

Apparatus. The apparatus (Figure 1) consists of a solution storage tube of about 115-ml. capacity and a tube packed tightly with copper ribbon. The storage tube is provided with 3-way, 120° stopcocks at either end. The storage and absorption tubes are connected at their ends with heavy-walled rubber tubing, long enough so that one tube can be raised above the other.

The commercially available Chore Girl scouring pads are satisfactory as packing in the absorption tube. The copper ribbon should be cleaned by heating it momentarily in a gas flame, the copper oxide coating formed being dissolved subsequently after the copper is packed in the tube and treated with the ammoniacal ammonium chloride solution. According to Uhrig *et al.* (3), cleaning the copper with nitric acid is not satisfactory, as the copper becomes inactive after being used a short time.

Photelometer. The instrument must be capable of determining the transmission of light at approximately 640 millimicrons.
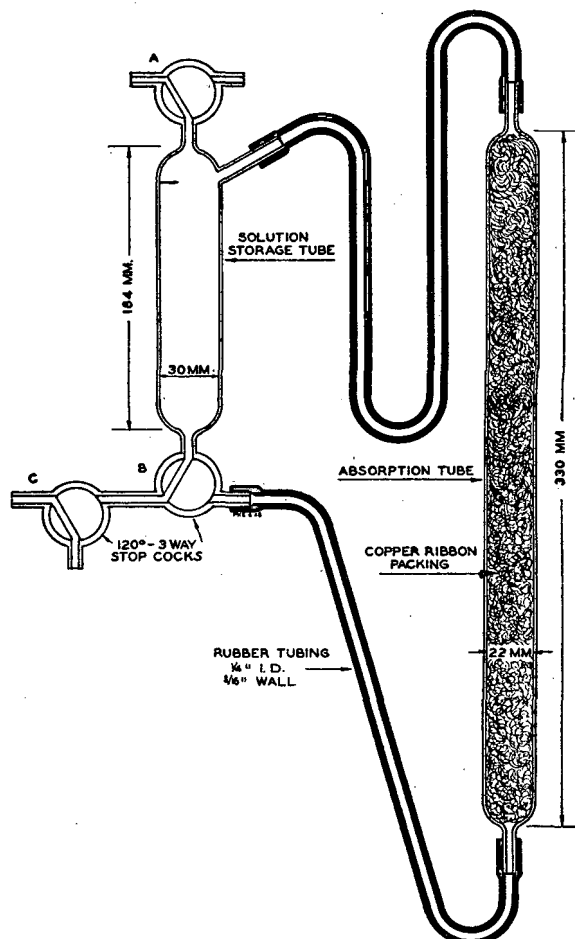

Figure 1. Apparatus for Determining Low Concentrations of Oxygen in Gas

PROCEDURE

Calibration of Photelometer. Accurately measure 5, 10, 15, 20, and 25 ml. of standard copper solution into separate 100-ml. volumetric flasks and make up to 100 ml. with ammonium hydroxide–ammonium chloride reagent. Mix well and determine the optical density at approximately 640 millimicrons, compared to the ammonium hydroxide–ammonium chloride reagent. From these results, prepare a graph showing the relationship between optical density and the milligrams of copper contained in 100 ml. of solution.

Operation of Apparatus. Determine the volume of the solution storage tube to a mark placed near its top. Determine the volume of solution that is retained by the copper packing after the absorption tube is filled with solution and allowed to drain for several minutes.

Assemble the apparatus as shown in Figure 1 and purge it with an inert gas. A small amount of oxygen in the gas is of no consequence. Connect the delivery tube of the reagent bottle to the left arm of stopcock A, and set the stopcock plug so that solution can be purged out of the right arm. Discharge enough solution to clear the tubing and stopcock of oxygen. Set stopcocks A and B so that solution can be introduced and retained in the solution storage tube. Fill this tube to the mark by allowing the gas in the tube to be displaced through the absorption tube out of one of the arms of stopcock C. Close A and C and set B so that the solution in the storage tube can pass into the absorption tube.

Raise the bottom of the solution storage tube above the top of the absorption tube, and allow the solution to fill the absorption tube, then invert the apparatus and allow the solution to pass back to the solution storage tube. Return the apparatus to its original position, and repeat the operation twice more. The solution must pass through the absorption tube and not merely in and out.

These operations remove all the oxygen from the gas within the apparatus and leave an atmosphere that is absolutely oxygen-free. Store all the solution in the apparatus in the absorption tube and set stopcocks B and C so that all the solution can be discharged through one of the side arms of C. Introduce fresh solution into the solution storage tube, wash the copper packing with this fresh solution, and discard it in a like manner. Repeat the washings until the solution, when it is taken from the apparatus and air is bubbled through it, has no color or only a slight constant color due to the oxygen in the reagent, and retain it as a blank.

The apparatus is now ready for use. Fresh solution is in the solution storage tube and the absorption tube is empty. If the gas contains hydrogen sulfide or mercaptans, pass it through a scrubber containing silver nitrate solution. Then introduce the gas to be analyzed through the left side arm of stopcock C, and allow it to flow for a few moments out of the bottom side arm. Set C and A so that the gas can pass through the absorption tube and out of the right side arm of A. Allow a small amount of solution to run into the rubber tubing between B and the absorption tube. This solution saturates the gas bubbling through it and prevents the gas from drying the copper packing. Meter the gas with a meter placed downstream from the apparatus, and pass the gas through the apparatus at a rate not to exceed 350 ml. per minute. The quantity of gas to pass is given in Table I

Table I. Gas Passed through Apparatus

Oxygen in Sample, %	Sample, Ml.
0.5 to 2.5	Fill storage tube
0.08 to 0.5	600
0.02 to 0.08	2,800
0.004 to 0.02	11,000
0.0008 to 0.004	55,000
0.0002 to 0.0008	280,000

Where the gas contains from 0.5 to 2.5% oxygen fill only the storage tube with gas, by first passing all the solution in the apparatus into the absorption tube and setting stopcocks B and A so that the gas passes through the storage tube. Pass enough gas through the tube to collect a representative sample, and use this sample, equal to the volume of the storage tube, for the analysis.

After the prescribed volume of gas has been passed through the apparatus, close A and C and set B so that the solution can be cycled through the absorption tube. Cycle the solution through the absorption tube at least three times, store it in this tube, and then discharge it from the apparatus while introducing fresh solution into the storage tube. Bubble air through the solution taken

from the apparatus until the color of the solution reaches its maximum density. Determine the optical density of this solution at 640 millimicrons, setting the photelometer to 100% transmission on the blank solution.

Calculations. The per cent oxygen in the gas analyzed is given by substituting in the following equation:

$$O = \frac{0.099\, C\, (S + h)}{V}$$

where
O = volume per cent oxygen in gas
C = milligrams of copper per 100 ml. of test solution obtained from optical density measurement and calibration graph
S = milliliters of solution in solution storage tube
h = milliliters of solution held up on copper packing
V = milliliters of gas sample

Accuracy. The copper-oxygen conversion factor is defined as the milliliters of pure oxygen at 0° C. and 760 mm. of mercury pressure equivalent to 1 mg. of copper and is theoretically equal to 0.088 ml. corresponding to the formation of cuprous oxide. Apparently some cupric oxide is also formed by carrying out the described procedure, and by introducing known volumes of oxygen into the apparatus, an average factor of 0.099 was obtained. The results of several such tests are shown in Table II. The maximum deviation from the average factor is 2.4%. MacHattie *et al.* (*1*) obtained an average factor of 0.0956, and Uhrig *et al.* (*3*) obtained results that indicated the reduction of any cupric oxide formed to cuprous oxide. However, the authors by limited tests were not able to duplicate the findings of Uhrig *et al.*

Table II. Determination of Oxygen Equivalent per Milligram of Copper

O_2 at 0° C. and 760 Mm. Ml.	Optical Density of Solution	Copper Mg./100 ml.	Factor to Convert Mg. Cu to Ml. O_2
2.44	0.335	24.6	0.099
2.43	0.330	23.9	0.102
1.01	0.135	10.1	0.100
1.01	0.140	10.4	0.097
1.51	0.205	15.4	0.098
1.51	0.205	15.4	0.098
		Av.	0.099

To fix the rate for the complete absorption of oxygen from a gas passed through the absorption tube, a second apparatus was constructed and nitrogen containing about 0.02% oxygen was passed through the two apparatus in series at various rates. At a rate of 350 ml. of gas per minute no oxygen was absorbed from the gas by the second apparatus in series. The results obtained from introducing known quantities of oxygen into the apparatus indicate that if the above rate is not exceeded the method is probably accurate to within at least 2.5% of the true value.

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Identification of Amidone

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Amidone may be identified microchemically by the formation of crystals with a series of reagents. Tests with zinc chloroiodide, potassium bromobromide, potassium iodoiodide, mercuric bromide, cadmium iodide, and Marmé reagent have been found suitable. A group of amidone precipitant reagents are proposed for macrotesting.

AMIDONE (6-dimethylamino-4, 4-diphenyl-3-heptanone), variously known as Methadone, Dolophine, Adanon, 10820, and AN-148, is a new synthetic drug introduced by the German chemical industry as a substitute for morphine.
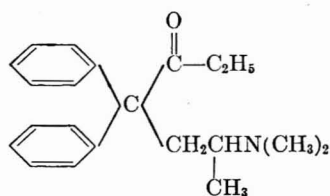
Amidone (base)

The hydrochloride of amidone is a white crystalline substance soluble in water to the extent of about 5.0%. Amidone is a racemate and has been resolved into its levo and dextrorotary isomers. Because this drug causes and supports addiction, it may be classified as a narcotic (2).

MICROCHEMICAL METHODS

The natural alkaloids and many synthetic alkaloidlike compounds can be identified microscopically by a variety of crystalline forms which they produce with alkaloidal reagents. A number of publications describe specific microcrystalline forms useful in the identification of very minute quantities of these substances (1, 3–7).

The growth of crystalline forms and their final size and shape may be controlled in various ways. To obtain reproducible crystals it is necessary to observe carefully exact procedures, which are often entirely empirical.

Method 1. Place a drop of a very dilute solution of amidone hydrochloride on a microscope slide. Put a drop of the appropriate reagent next to it on the slide, and draw the drops together with a small glass rod. Place a cover glass over the precipitate; this serves to prevent evaporation, as some of the crystals are formed rather slowly. If necessary, use a drop of liquid petrolatum to ring the cover glass. Such a protected slide will remain useful for several days and is important when photomicrographs are contemplated. Allow the preparations to stand until characteristic crystals are formed.

Method 2. In a method which works well with zinc chloroiodide reagent dry amidone is placed on a microscope slide. If a solution is to be tested directly, evaporate it carefully to dryness on the glass slide and place a drop of reagent over the dried material. Crystal forms develop gradually. These are usually enhanced in size and crystal structure over those obtained by the instantaneous precipitations caused by mixing solutions directly to each other. The crystal forms will differ with varying techniques and therefore comparable tests should be made with known samples of amidone hydrochloride.

Reagents and Micro Tests. ZINC CHLOROIODIDE REAGENT. Dissolve 20 grams of zinc chloride in 10 ml. of distilled water. Add a solution of 2.1 grams of potassium iodide, 0.1 gram of iodine dissolved in 5.0 ml. of distilled water, and a small crystal of iodine.

After addition of the reagent, a precipitate of black droplets forms around the solid amidone particles, if method 1 is used. The droplets disappear and at first dark opaque tabular crystals are often formed. These crystals eventually disappear also and the characteristic crystals shown in Figure 1, *B*, are formed. If the amidone is in solution and method 2 is used, a second type of crystal is formed, as shown in Figure 1, *A*. No intermediate crystal form has been obtained by the second method.

POTASSIUM IODOIODIDE REAGENT. Dissolve 1.5 grams of potassium iodide and 0.5 gram of iodine in a small amount of water. When solution is complete, dilute to 125 ml.

Figure 2 (left) shows the type of crystalline rosettes formed when method 1 is used. Under high magnification the crystal forms look like small winged insects. The first precipitate of black droplets disappears as the more stable crystalline forms appear.

POTASSIUM BROMOBROMIDE REAGENT. To 10.0 ml. of a saturated bromine solution in distilled water add 2.0 grams of potassium bromide.

A drop of very dilute amidone solution is used, with method 1. Concentrated solutions precipitate out in a solid mass. This reaction is very sensitive to small amounts of amidone. When the reagent has been added a whitish precipitate forms. Later crystals and rosettes, formed by rays of crystals, begin to grow. Figure 2 (right), shows the individual crystals, which are typically flat with keylike structures at each end.

MERCURIC BROMIDE REAGENT, a saturated solution of mercuric bromide in cold distilled water.

Method 1 is used with this reagent. Crystallization begins immediately and the reaction is sensitive to small amounts of amidone. Typical groups, usually shaped like children's jacks, are often formed in straight or curved linear rows. (Figure 3, left).

MARMÉ REAGENT. Dissolve 3.0 grams of cadmium iodide in 18.0 ml. of distilled water containing 6.0 grams of potassium iodide. This reagent precipitates with low concentrations of amidone hydrochloride. A milky-white precipitate is formed, which after some time crystallizes into characteristic irregular flat-winged rosettes. Some of these rosettes look like tiny flies (Figures 3, right, and 4, left).

CADMIUM IODIDE REAGENT, a saturated solution of cadmium iodide in cold distilled water.

Method 1 is used, and a milky-white precipitate is formed immediately. Later crystallization begins and the crystals formed
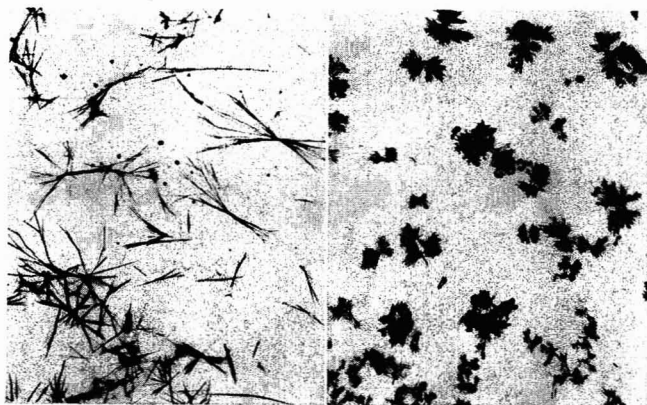

A   B

Figure 1. Amidone (70 ×)

Zinc chloroiodide reagent
A. Reagent added to dry material
B. Reagent added to solution of amidone

A   B

Figure 2.   Amidone (135 ×)

A. **Potassium iodoiodide reagent**
B. **Potassium bromobromide reagent**

are irregular feathery-winged rosettes, often with unequal branches (Figure 4, right).

Comparable tests with the same reagents and demerol, 1-methyl-4-phenylpiperidine-4-carboxylic acid ethyl ester, gave precipitations in all cases. With the exception of Marmé reagent, no crystal forms were noted even after several hours. The Marmé preparation crystallized out around the edges of the cover glass, showing well formed dendritic flattened crystal forms, which have no comparable resemblance to the crystals obtained with amidone and this reagent.

With morphine sulfate similar comparative tests were made. Marmé reagent gave a heavy white precipitate and immediate formation of very long thin hairlike matted crystals. Cadmium iodide reagent gave characteristic many-branched rosettes with thin hairlike radiates. Potassium bromobromide reagent gave a few rosettes showing flat lathlike radiates. Potassium iodoiodide reagent gave an immediate bulky brown precipitate. Later the

well-known characteristic flat, feathery, red-branching crystals were formed. The remaining reagents gave no crystalline forms. None of the crystals obtained with morphine in any way resembled the corresponding amidone crystals.

MACROCHEMICAL TESTS

The reagents given in the previous section are used. The following additional reagents can be utilized:

Cobalt thiocyanate a 2.0% solution in distilled water.
Bromine water, a saturated solution in distilled water.
Concentrated aqueous ammonium hydroxide.
Mayer's reagent.
Sodium hydroxide, 1.0% in distilled water.
Lime water, a saturated solution in distilled water.

A   B

Figure 3.   Amidone (70 ×)

A. **Saturated mercuric bromide reagent**
B. **Marmé reagent**

Table I.   Precipitation Reactions

|	Marmé Reagent	Zinc Chloroiodide Reagent	Potassium Bromoiodide Reagent	Potassium Iodoiodide Reagent	Cadmium Iodide Reagent	Mercuric Bromide Reagent	Cobalt Thiocyanate, 2.0%	Bromine Water (Saturated)	Concentrated NH₄OH	Mayer's Reagent	NaOH, 1.0%	Lime-Water (Saturated)
Amidone	Heavy milky-white ppt.	Heavy flocc. yellowish ppt.	Yellow ppt.	Heavy brown ppt. re-dissolves	Heavy white ppt.	White ppt.	Heavy blue ppt. redissolves in H₂O	Very heavy light yellow ppt.	Heavy white ppt.	Heavy yellowish-white ppt.	Opalescent white ppt.	Opalescent white ppt.
Demerol	Heavy milky-white ppt.	Light yellowish flocc. ppt.	No ppt.	Heavy dark-brown ppt.	No ppt.	No ppt.	No ppt.	Deep yellow ppt. re-dissolves	No ppt.	Heavy yellowish white ppt.	No ppt.	No ppt.
Morphine sulfate	No ppt.	Light white flocc. ppt.	No ppt.	Brown ppt., dis-perses or redis-solves	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	Flocc. trans-parent ppt.	No ppt.	No ppt.
Codeine sulfate	Heavy milky-white ppt.	Light flocc. ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	Heavy yellowish white ppt.	No ppt.	No ppt.
Heroin hydro-chloride (tablets)	No ppt.	Light yellow flocc. ppt.	No ppt.	Heavy red-brown ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.
Cocaine hydro-chloride	Heavy milky-white ppt.	Heavy brown flocc. ppt.	Heavy canary yellow ppt.	Heavy brown ppt.	Heavy white ppt.	White ppt. redis-solves	No ppt.	Heavy orange ppt.	Heavy white ppt.	Heavy yellowish ppt.	White ppt.	White ppt.
Procaine	Heavy milky-white ppt.	Light yellow flocc. ppt.	Heavy yellow ppt.	Heavy brown ppt.	No ppt.	No ppt.	No ppt.	Heavy yellow ppt.	No ppt.	Heavy yellowish white ppt.	No ppt.	No ppt.
Dionine (ethyl morphine hydro-chloride)	No ppt.	Light yellow flocc. ppt.	Yellow ppt.	Heavy brown ppt.	No ppt.	No ppt.	No ppt.	Heavy orange ppt.	No ppt.	Heavy yellowish ppt.	No ppt.	No ppt.
Narceine hydro-chloride	No ppt.	Slight yellowish ppt.	Heavy yellow ppt.	Heavy brown ppt.	No ppt.	No ppt.	No ppt.	Yellow ppt.	No ppt.	Light flocc. yellowish ppt.	No ppt.	No ppt.
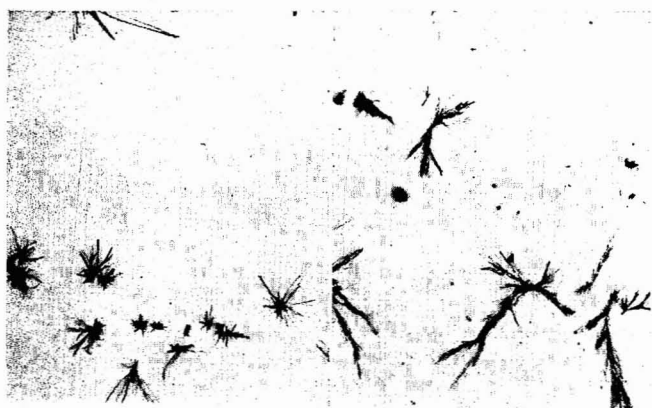
Figure 4. Amidone (70 ×)

A. Marmé reagent
B. Saturated cadmium iodide reagent

All the tests tabulated were made with approximately 0.1% solutions of the alkaloid or alkaloidlike compounds. Each substance was dissolved in about 5.0 ml. of distilled water and the

reagent was added. The only exception was the test with cobalt thiocyanate, which required a relatively high concentration of amidone. To 0.5 ml. of a 1% solution of amidone about 1.0 ml. of the reagent was added. If distilled water is added to the blue precipitate, it dissolves to give an almost colorless solution and is a good confirmative test.

Table I gives the precipitation reactions of twelve reagents with amidone and compares them with the similarly treated demerol, morphine sulfate, codeine sulfate, heroin hydrochloride, cocaine hydrochloride, procaine, dionine, and narceine hydrochloride.

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Cadmium in Biological Materials and Foods

Dithizone Method for Evaluating Minute Quantities

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A dithizone procedure for evaluating minute amounts of cadmium is presented. The interfering ions of copper and mercury, and most of those of cobalt and nickel are extracted as dithizonates with carbon tetrachloride directly from an acidified aqueous solution of the sample. The aqueous phase is retained and made alkaline with an ammonium hydroxide–ammonium citrate buffer solution containing Rochelle salt, and interference of remaining cobalt and nickel is eliminated by adding dimethylglyoxime and extracting with chloroform. Again the aqueous phase is retained and sufficient sodium hydroxide added to make a 5% solution. Cadmium is extracted as the dithizonate in carbon tetrachloride and evaluated photometrically. The proposed procedure compares favorably in sensitivity with that claimed for published dithizone methods for determining small amounts of cadmium, and possesses the following additional advantages: It removes interfering copper and other acid-stable dithizonates directly from the acidified aqueous solution of cadmium, it effectively eliminates interference by cobalt and nickel, it provides protection for the cadmium dithizonate against light effects by using amber glassware, it requires only one separatory funnel per determination, and it is less time-consuming.

FISCHER and Leopoldi (4) proposed a dithizone (diphenylthiocarbazone) method for the determination of cadmium in metals. The cadmium dithizonate was extracted with carbon tetrachloride from a 5% sodium hydroxide aqueous solution of the sample. Hydrochloric acid was added to the carbon tetrachloride extract to decompose the cadmium dithizonate and the liberated dithizone was evaluated photometrically. These authors reported that the determination could be made in the presence of all ions except those of copper, silver, gold, mercury, palladium, nickel, and cobalt. Cholak and Hubbard (1) developed a method involving the use of dithizone and its analog, di-β-naphthylthiocarbazone, for the removal of interfering ions and the evaluation of cadmium in biological material. They compared results by this method with those obtained by both spectrographic and polarographic procedures and found the dithizone method the most sensitive but also the most laborious and time-consuming. Klein and Wichmann (3) applied a dithizone technique to the analysis of cadmium in biological materials and foods and obtained satisfactory results; however, when their procedure was submitted for collaborative study (6) difficulty was encountered by the collaborators.

The writers found, as pointed out by Fischer and Leopoldi (4), that cadmium dithizonate can be extracted quantitatively with carbon tetrachloride from a 5% solution of sodium hydroxide; however, the remainder of the technique is inadequate when applied to biological materials because it does not provide for the elimination of interference by such common ions as lead, zinc, copper, mercury, cobalt, and nickel. The high pH of the solution from which the cadmium is extracted will prevent interference by lead and zinc, unless they are present in excessive amounts, but copper, mercury, nickel, and cobalt, if not completely removed before the final extraction of the cadmium, will be evaluated as cadmium.

Customarily in cadmium dithizone procedures all the ions reacting with dithizone are extracted with carbon tetrachloride or chloroform from a buffered (pH 8 to 9) ammoniacal solution of the sample. The extract of metallic dithizonates is then treated with aqueous hydrochloric acid which decomposes the dithizonates of cadmium, zinc, and lead, and some of the cobalt and nickel. These ions enter the aqueous phase and the carbon tetrachloride solution is discarded, thereby separating copper, mercury, and much of the cobalt and nickel from the cadmium. The acidi-

fied aqueous solution containing the cadmium is treated with some tartrate salt and sufficient sodium hydroxide to give a 5% concentration of alkali and the cadmium is extracted with a carbon tetrachloride solution of dithizone (1, 3, 6). Klein and Wichmann (8), rather than evaluate the cadmium dithizonate in the carbon tetrachloride solution at this point, reacidified the solution and re-extracted it in an attempt to remove any nickel or cobalt that was not removed during the initial extraction. They then made the cadmium solution alkaline again and extracted the cadmium dithizonate for colorimetric evaluation. This procedure requires several separatory funnels per determination and obviously is time-consuming.

The writers have investigated various techniques for eliminating interference by other ions when dithizone is used for the colorimetric evaluation of cadmium. This paper presents the results of this investigation and describes an improved method for evaluating minute amounts of cadmium such as occur in in biological materials and foods.

OUTLINE OF METHOD

The principal steps in the method are: (1) preparing an acidified aqueous solution (pH 2.0 to 2.3) of the sample, (2) extracting an aliquot of this solution with a carbon tetrachloride solution of dithizone to remove the interfering ions of copper and mercury, and most of those of cobalt and nickel, (3) making the aqueous phase alkaline (pH 8.5 to 9.0) with an ammonium hydroxide–ammonium citrate buffer solution containing Rochelle salt, adding dimethylglyoxime and extracting with chloroform to eliminate interference by the cobalt and nickel not removed in step 2, (4) adding sodium hydroxide to the aqueous phase to make approximately 5% alkali and extracting with a carbon tetrachloride solution of dithizone to remove the cadmium as the dithizonate, and (5) evaluating photometrically the amount of cadmium present.

REAGENTS

Except as indicated, c.p. or reagent grade chemicals were found satisfactory without further purification.

Approximately normal solution of sulfuric acid. Normal solution of hydrochloric acid. Normal solution of ammonium hydroxide. Solution of sodium hydroxide 20 grams 100 ml. per chloroform.

Carbon tetrachloride used in this procedure was satisfactory for reuse when recovered by the method recommended by Cowling and Miller (2).

Dithizone (Diphenylthiocarbazone) Solution in Carbon Tetrachloride (2). Dissolve 0.2 gram of dithizone in 500 ml. of carbon tetrachloride and filter to remove insoluble matter. Place the solution in a 5-liter separatory funnel, add 2 liters of 0.02 N ammonium hydroxide (dilute 40 ml. of the N solution), and shake to extract the dithizone into the aqueous phase. Separate the phases, discard the carbon tetrachloride phase, and extract the ammoniacal solution of dithizone with 100-ml. portions of carbon tetrachloride until the carbon tetrachloride extract is a pure green color. Discard the carbon tetrachloride phase after each extraction. Add 500 ml. of carbon tetrachloride and 45 ml. of N hydrochloric acid, and shake to extract the dithizone into the carbon tetrachloride. Separate the phases and discard the aqueous phase. Dilute the carbon tetrachloride solution of dithizone to 2 liters with carbon tetrachloride and mix. Store the reagent in a brown bottle out of direct sunlight.

Ammonium Hydroxide–Ammonium Citrate Buffer Solution Containing Rochelle Salt. Dissolve 113 grams of ammonium citrate, $(NH_4)_2HC_6H_5O_7$, and 266 grams of Rochelle salt, $KNaC_4H_4O_6.4H_2O$, in 4 liters of distilled water. Add concentrated ammonium hydroxide until a pH of 8.5 to 9.0 is obtained (approximately 40 ml.). Place the solution in a large separatory funnel, add an excess of dithizone in chloroform solution, prepared by dissolving 0.1 gram of dithizone in 200 ml. of chloroform and filtering, and shake the mixture vigorously. An excess of dithizone is indicated if the aqueous layer has an orange-yellow coloration after the phases have separated. Draw off and discard the chloroform layer. Extract the aqueous phase with chloroform until the dithizonates and excess dithizone are removed, as indicated by the chloroform extract becoming colorless. Store the aqueous phase in a Pyrex vessel.

Dimethylglyoxime Reagent (9). Dissolve 2.0 grams of dimethylglyoxime in 250 ml. of dilute ammonium hydroxide (10 ml. of concentrated ammonium hydroxide diluted to 250 ml.), filter, and dilute to 1 liter with distilled water.

Standard Cadmium Solution (8). Prepare a stock solution containing 1 mg. of cadmium per ml. by dissolving 1 gram of the pure metal in 20 to 25 ml. of concentrated hydrochloric acid with warming and diluting to 1 liter. Prepare an intermediate standard solution containing 100 micrograms of cadmium per ml. by diluting an appropriate quantity of the stock solution. A convenient final standard solution contains 2 micrograms of cadmium per ml. Add 5 ml. of concentrated hydrochloric acid per liter before diluting the final solution to volume in order to stabilize the solution.

EQUIPMENT

A 5-liter separatory funnel; 125-ml. Squibb type separatory funnels made of amber or low actinic glass, and 25-ml. volumetric flasks made of amber or low actinic glass. A separatory funnel rack. A photoelectric colorimeter or spectrophotometer. The method is adaptable to any suitable photoelectric colorimeter or spectrophotometer. Platinum dishes.

PROCEDURE

Preparation of Solution of Sample. Place a sample of suitable size, depending upon its nature and cadmium content, in a platinum dish. Samples containing 5 to 10 grams of dried material have usually been found satisfactory. Add 25 ml. of approximately 2 N sulfuric acid and evaporate to dryness. Ash in an electric muffle furnace at 550° C. Add 10 ml. of 1 N hydrochloric acid to the dish and heat to dissolve all acid-soluble ash. Filter through an acid-washed filter paper into a 100-ml. volumetric flask. Wash the dish and filter paper containing the undissolved ash with hot water until the filtrate is no longer acid. Allow the contents of the flask to cool. Add a drop of methyl red indicator and neutralize the acid with 1 N ammonium hydroxide. Add 4 ml. of 1 N hydrochloric acid and dilute to 100 ml. with distilled water. Use aliquots of this solution for analysis.

Removal of Copper, Mercury, and Part of Cobalt and Nickel. Pipet an aliquot of the ash solution containing not more than 20 micrograms of cadmium into a 125-ml. amber glass separatory funnel. Add 1 ml. of 0.2 N hydrochloric acid for each 5 ml. of ash solution less than 10 ml. taken or 1 ml. of 0.2 N ammonium hydroxide for each 5 ml. over 10 ml. taken. Add 10 ml. of dithizone reagent in carbon tetrachloride and shake vigorously for 1 minute. Permit the layers to separate and discard the carbon tetrachloride layer. (Allow at least 3 minutes for phases to separate after each shaking period throughout this procedure.) Add 10 ml. more of reagent and shake 1 minute. Allow the layers to separate and discard the carbon tetrachloride layer. Repeat shakings and extractions as above until all acid-stable dithizonates are removed. Removal is judged to be complete when the carbon tetrachloride layer shows only the normal green color of dithizone. Remove excess dithizone from the aqueous layer by extracting twice with 6- to 8-ml. portions of carbon tetrachloride, using 10-second shaking periods.

Elimination of Interference by Remaining Nickel and Cobalt with Dimethylglyoxime. Add 45 ml. of the ammonium hydroxide–ammonium citrate reagent containing Rochelle salt, 5 ml. of dimethylglyoxime reagent, and 15 ml. of chloroform. Shake vigorously for 1 minute, allow layers to separate, and draw off and discard the chloroform layer. Add 10 ml. of chloroform and shake 30 seconds. Allow layers to separate, draw off chloroform, and discard. Add 5 ml. of carbon tetrachloride and shake 10 seconds. Allow layers to separate, draw off carbon tetrachloride, and discard.

Extraction and Evaluation of Cadmium as Dithizonate. Add to the aqueous phase 25 ml. of 20% sodium hydroxide and 10 ml. of dithizone reagent in carbon tetrachloride. Shake vigorously 1 minute. Allow layers to separate. Draw off the carbon tetrachloride layer into a 25-ml. amber colored volumetric flask. Add 4 to 5 ml. of carbon tetrachloride to the separatory funnel and shake vigorously 15 seconds. Allow layers to separate and draw off the carbon tetrachloride layer into the volumetric flask. Shake the aqueous layer in the separatory funnel twice more with 4 to 5 ml. of carbon tetrachloride as directed above and each time draw off the carbon tetrachloride into the volumetric flask. Dilute to volume with carbon tetrachloride and mix. Read per cent of light transmitted on some suitable photoelectric colorimeter or spectrophotometer within 30 minutes after the extraction is completed. With a photoelectric colorimeter use a Corning Sextant Green No. 401 light filter or its equivalent. With a spectrophotometer use a wave-length setting of 515 millimicrons. Determine the amount of cadmium in the aliquot analyzed by use of a reference

curve relating per cent of light transmitted and concentration of cadmium.

Preparation of Reference Curve. Add 0, 2.5, 5, 10, 15, and 20 micrograms of cadmium, respectively, to amber glass 125-ml. separatory funnels and adjust volume to 25 ml. with distilled water. Carry through entire procedure for evaluation of cadmium as recommended for acid solutions of sample. Plot per cent of light transmitted against micrograms of cadmium on semilogarithmic paper. Figure 1 shows a typical standard reference curve obtained with known quantities of cadmium carried through the entire procedure. The per cent of light transmitted was measured with a Cenco-Sheard-Sanford photelometer using a Corning No. 401 Sextant Green light filter of 6.00-mm. thickness (obtained by using together a filter of standard thickness and one of half standard thickness) and a 1-cm. solution cell. Such curves could be readily duplicated with given batches of reagents.

EXPERIMENTAL

Spectral Characteristics of Cadmium Dithizonate. Twenty micrograms of cadmium were carried through the entire procedure of analysis and the cadmium dithizonate obtained in carbon tetrachloride solution was tested for per cent light transmitted with a Cenco-Sheard spectrophotelometer through the wave-length range from 400 to 700 millimicrons. Maximum absorption of light occurred at 515 millimicrons. The spectral transmittance curve obtained is shown in Figure 2.

Use of Amber Glassware to Protect Cadmium Dithizonate from Light Effects. Table I shows a comparison of the efficiency of amber and plain glassware in protecting cadmium dithizonate in carbon tetrachloride solution against decomposition when exposed to fluorescent and direct sunlight. Preparation of the solutions was carried out in fluorescent light, and in all cases the initial readings for the per cent light transmitted were made within 30 minutes after extraction of the cadmium dithizonate into carbon tetrachloride. The data show (1) that the solutions of cadmium
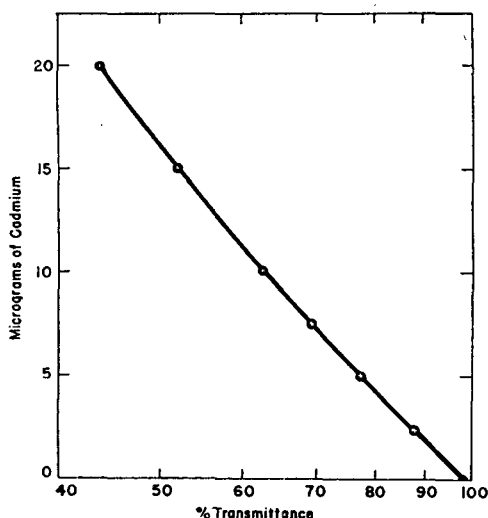
dithizonate gave practically the same initial transmittance readings whether contained in amber or plain glassware, (2) an additional 30 minutes of exposure to either fluorescent light or sunlight resulted in less decomposition in amber than in plain glassware, and (3) amber glassware aided particularly in the protection of the blank solution against light effects.

Application of Procedure. Table II shows the efficiency of the method for evaluating cadmium in synthetic solutions containing zinc, lead, copper, mercury, cobalt, and nickel. Five hundred micrograms of zinc in an aliquot analyzed caused no indication of apparent cadmium and 1000 micrograms produced only a 0.2-microgram interference. Klein (7) has found that 2 and 3 mg. of zinc simulate 0.6 and 1.2 micrograms of cadmium, respectively, by this method. Hence, in the cases of materials such as oysters and molasses, which may contain as much as 0.5 to 2 mg. of zinc per gram (5, 7), precautions must be taken to select an aliquot which does not contain more zinc than can be tolerated. Klein and Wichmann (8) reported that 10% alkalinity would decrease the interference of high zinc concentrations. Lead did not interfere when present in an aliquot up to 500 micrograms. Interferences by copper, mercury, cobalt, and nickel were all prevented completely when each was present to the extent of 100 micrograms. Satisfactory analyses of known amounts of cadmium were obtained in synthetic mixtures which contained as much as 100 micrograms of each of the above interfering ions in the aliquots analyzed. Such mixtures, however, required a large quantity of the dithizone reagent to remove all the interfering ions extractable in the acid extraction step of the method.
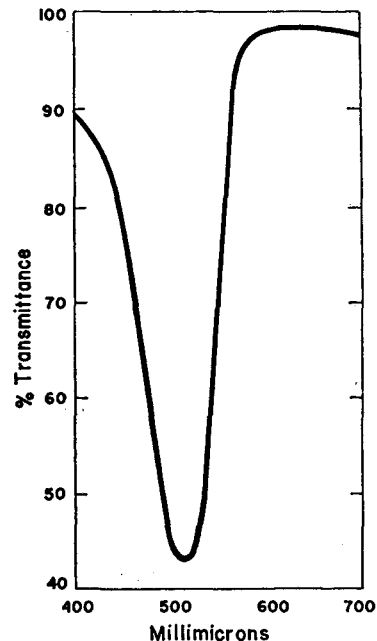

Figure 2. Spectral Transmittance Curve

Figure 1. Reference Curve

Table I. Protection of Cadmium Dithizonate from Light by Use of Amber Glassware

Type of Light	Micrograms of Cd per 25 Ml. of CCl₄	Color of Glassware	Initial reading	After 30-min. exposure	Difference
Fluorescent	0	Amber	98.5	98.5	0.0
	0	Plain	98.5	99.4	0.9
	5	Amber	80.0	80.9	0.9
	5	Plain	80.2	82.0	1.8
Direct sunlight	0	Amber	98.8	98.8	0.0
	0	Plain	98.8	99.5	0.7
	5	Amber	80.0	83.0	3.0
	5	Plain	80.3	85.5	5.2

Table II. Analysis of Cadmium in Synthetic Solutions

	Present, Micrograms						Cd Found,
Cd	Zn	Pb	Cu	Hg	Co	Ni	Micrograms
0	500	...	...	...	...	...	.0
0	1000	...	...	...	...	...	0.2
0	...	500	...	...	...	...	.0
0	...	...	100	...	...	...	0.0
0	...	...	...	100	...	...	0.0
0	...	...	...	...	100	...	0.0
0	...	...	...	...	...	100	0.0
0	50	50	50	50	50	50	0.0
2.5	25	25	25	25	25	25	2.5
5.0	100	100	100	100	100	100	5.0
15.0	50	50	50	50	50	50	14.8

Table III indicates the precision of the method when applied to the determination of cadmium in plant materials. Various sized samples of spinach, lettuce, and alfalfa leaf meal were ashed and analyzed. The results obtained show good agreement for amounts of cadmium present. Spectrographic analysis of acid solutions of the ash of these plant materials indicated qualitatively that cadmium was present in all cases.

Table III. Cadmium Found in Plants Using Different Weights of Samples

Plant	Sample, Grams	Cd, P.P.M.
Spinach (dried)	1.0	1.0
	3.0	1.2
	5.0	1.2
Lettuce (dried)	1.0	0.4
	5.0	0.4
	5.0	0.5
Alfalfa leaf meal	2.5	0.1
	10.0	0.2

Table IV. Determination of Cadmium in, and Recovery of Cadmium Added to, Biological Materials and Foods

Samples Analyzed	Amount of Sample, Grams	Cadmium in Aliquots[a]		
		Added	Present	Found
Spinach (dried)	5.0	0	...	0.6
		2.5	3.10	2.7
	1.0	0	...	0.1
		5.0[b]	5.1	5.2
Lettuce (dried)	5.0	0	...	0.3
		2.5	2.8	2.6
		5.0[b]	7.6	7.7
Alfalfa leaf meal	10.0	0	...	0.2
		2.5	2.7	2.2
		5.0[b]	7.2	7.1
Lamb liver	20.0	0	...	0.3
		2.5	2.8	2.8
	Ml.			
Canned tomato juice	50.0	0	...	0.2
		2.5	2.7	2.7
Canned grapefruit juice	50.0	0	...	0.1
		2.5	2.6	2.5
Canned orange juice	50.0	0	...	0.1
		2.5	2.6	2.5
Human urine	70.0	0	...	0.1
		2.5	2.6	2.5
	Grams			
Human feces	15.0	0	...	0.2
		2.5	2.7	2.2

[a] Ash extracts diluted to 100 ml. and 10-ml. aliquots used in all cases.
[b] Cadmium added to extracts of ash; in all other cases cadmium added to sample before ashing.

Table IV shows results obtained when the procedure was applied to the determination of cadmium in various biological materials and foods, and the recovery of known amounts of added cadmium. The amounts of cadmium found in all products analyzed were very small. The recovery of cadmium added before ashing was fairly satisfactory. Recoveries of ±0.1 microgram of cadmium were obtained in all cases where the cadmium was added after ashing. With the plant materials and feces some cadmium is indicated to have been lost in the ashing process or in the leaching of the cadmium from the ash residue.

DISCUSSION AND SUMMARY

The extraction of acid-stable dithizonates directly from the acidified solution of the sample with a carbon tetrachloride solution of dithizone was found satisfactory in every type of material analyzed. This shortens an otherwise time-consuming and laborious procedure, and also makes possible the use of a single separatory funnel per determination, which facilitates manipulation and increases accuracy of results obtained.

Extraction of acid solutions of the ions with dithizone was found to be inadequate for eliminating interference by nickel and cobalt, especially when appreciable amounts of these cations were present. In the authors' experience the most effective means of preventing interference by these ions was to make the solution ammoniacal, add dimethylglyoxime, and follow with a chloroform extraction to remove nickel dimethylglyoxime. Apparently the dimethylglyoxime forms a derivative of cobalt which is not extractable with chloroform but is stable in the presence of dithizone in 5% sodium hydroxide, thereby preventing it from interfering with the determination of cadmium.

No work was done in this study to determine the extent of interference by gold, silver, palladium, bismuth, and tin, as they should seldom occur in appreciable quantities in biological materials. However, even if they were present in small quantities their interference should be eliminated by the procedure, since

Fischer (3) reported that a dithizone extraction at a pH of approximately 2.3, as used in the first extraction, should extract the dithizonates of these cations. The limiting concentrations of magnesium or calcium phosphate that the method can tolerate were not determined. Although slight turbidity appeared in the aqueous phase with some samples at the high alkalinity of the cadmium extraction, no effect on efficiency of recovery of added cadmium from such samples was noted. Klein (7) observed that beyond 100 mg. of either magnesium or calcium phosphate precipitation occurred. He also suggested that such materials as dry skim milk and bones may have interfering quantities of phosphates if too large aliquots are taken for analysis.

The evaluation procedure gave excellent results when applied to synthetic mixtures of cadmium and interfering ions. Marked agreement in parts per million of cadmium present in plant materials was obtained when samples of varying size were analyzed. Recoveries within ±0.1 microgram of the known amounts of cadmium added were obtained in the analysis of the canned juices of tomatoes, grapefruit, and oranges, as well as with lamb liver and human urine. Less satisfactory recoveries of known amounts of cadmium added to dried spinach, lettuce, alfalfa leaf meal, and human feces were obtained. Previous workers, notably Cholak and Hubbard (1) and Klein and Wichmann (8), stated that cadmium is lost by volatilization in plain dry ashing of biological materials. They recommended wet-ashing procedures. However, as cadmium sulfate has a melting point of 1000° C. sulfuric acid was used in this investigation as a fixative for dry ashing at 550° C. Preliminary experiments indicated that such an ashing technique gave much lower blank values than the wet-ashing procedures. It is believed by the authors that in the cases of relatively low recoveries of added cadmium the cadmium was not volatilized during the ashing process used but the losses were due to the difficulty of leaching the cadmium from the large amount of acid-insoluble ash existing in these materials. The evaluation procedure was shown not to be at fault with these materials, as known amounts of cadmium added to the ash extracts were recovered within ±0.1 microgram in all cases.

The sensitivity of the procedure compares favorably with that claimed for published dithizone methods for determining small amounts of cadmium and possesses the following additional advantages: It removes acid-stable dithizonates directly from an acidified aqueous solution of cadmium, it provides a means of adequately separating nickel and cobalt from cadmium, it provides protection for the cadmium dithizonate against light effects by using amber-colored glassware, it requires only one separatory funnel per determination, and it requires less time for making the analysis.

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## Qualitative Analysis of Organosilicon Compounds and Polymers

Determination of Hydrocarbon Substituents

CHARLES A. BURKHARD AND FRANCIS J. NORTON, *General Electric Co., Schenectady, N. Y.*

WHEN the presence of silicon is established in an organic compound, the usual methods of organic qualitative analysis generally are insufficient to give adequate clues as to the possible identity and structure of the unknown compound, mixture, or polymer. Unlike acids, esters, and amines, the typical organosilicon compounds do not form solid class derivatives. It therefore becomes necessary to develop a scheme of qualitative analysis for this class of compounds.

This paper reports a method of establishing the identity of the monovalent hydrocarbon radicals attached directly to silicon.

Kipping (*1*) has observed that the silicon-phenyl bond is cleaved by acids to give benzene. This is a general reaction enabling one to cleave both aryl and alkyl groups from silicon.

$$R—Si\xrightarrow{\text{H}_2\text{SO}_4}RH$$
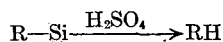
The hydrocarbon is identified by means of the General Electric mass spectrometer. It has been possible to recover as much as 70% of the total available methane from a polydimethyl siloxane polymer.

A 10- to 500-mg. sample of the unknown organosilicon compound is digested by heating with 10 to 15 ml. of concentrated (95%) sulfuric acid. The gaseous reaction products are collected in a gas buret and washed with aqueous sodium hydroxide to remove the carbon dioxide and sulfur dioxide. The gas sample, which is diluted with air, is then transferred to an evacuated bulb and placed in the sample train of the mass spectrometer. The entire sample is cooled with liquid nitrogen. After sufficient time has elapsed to cool the entire sample bulb thoroughly, a small sample of the gas, noncondensable by liquid nitrogen, is bled into the sample train. This small aliquot is allowed to enter into the sample system, then to flow through a calibrated leak into the

mass spectrometer. It is possible to detect hydrogen and methane in the presence of air. As only these two materials have sufficient vapor pressure to appear with the air when the sample is at liquid nitrogen temperature, about −195° C., it is possible to detect these compounds readily in the presence of the higher hydrocarbons.

After the presence or absence of hydrogen and methane has been established, the sample bulb is pumped to a pressure of 1 micron or less while still being cooled by liquid nitrogen. When the pumping has been completed, the sample is closed off, the liquid nitrogen is taken away, and the sample bulb is allowed to warm to room temperature. By this procedure, the methane, hydrogen, and components of air are completely eliminated from the sample bulb. The higher boiling hydrocarbons are then determined. Water will appear in the spectrum, as masses 16, 17, and 18, but it does not interfere. Total time consumed is about 15 to 30 minutes per sample.

The following radicals have been identified in organosilicon compounds: hydrogen, methyl, ethyl, butyl, amyl, cyclohexyl, and phenyl.

It is possible by this technique to differentiate between the silicon-hydrogen bond and the silicon-silicon bond. Both bonds are hydrolyzed by alkali to give hydrogen, but only the silicon-hydrogen bond reacts with acid to give hydrogen. In molecules where it is suspected that both silicon-hydrogen and silicon-silicon bonds are present, quantitative analysis data can be used simultaneously to confirm the presence of the silicon-silicon bond.

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A Hood for Work with Radioactive Isotopes

A. K. SOLOMON, *Harvard Medical School,* AND C. A. FOSTER, *Harvard University, Boston, Mass.*

A HOOD has been constructed for preliminary work with radioactive material as required for small scale chemical and biological experiments. Because it was necessary to design the hood in advance of any exact knowledge of the intensity of the sources that would be handled, it was decided arbitrarily to design it to accommodate sources of intensity equal to 500 millicuries of radium. To date, there has been no occasion to handle more than 50 mc. of radioactive material, and the design has accordingly been simplified and modified for these less stringent requirements without affecting its possible later use for intense sources. In view of the widespread use of radioactive isotopes, and the published description of the hazards involved in their use (*1-3*), it has seemed desirable to describe this installation.

Figure 1, a drawing of the hood as originally designed, shows the setup for the more intense sources; Figure 2 shows the hood as modified for low intensity sources.

The sides, back, and bottom of the hood are constructed of 8 inches of concrete and 0.5 inch of lead. The equivalent thickness

of the bottom is appreciably greater; in view of the oblique path the rays must take, the shielding is equivalent to approximately 12 inches of concrete plus the lead. The ceiling is also 8 inches thick, but has no lead because the floor of the story above is 5.5 feet above the top of the hood. The front of the hood is closed by 2.5 inches of lead, cast in steel frames.

Although the laboratory is on the ground floor, it was necessary to build concrete piers in the pipe space beneath it to support the 3.5-ton weight of the hood. Its position within the laboratory was chosen so that inverse square law protection would be available in addition to that provided by the concrete, as shown in Figure 3.

Special precautions were taken with the services that enter and leave the hood.

A removable stainless steel pan with a 1-inch turned-up lip rests on the bottom. Waste escapes through a stainless steel sink designed for removal and relatively easy replacement; it is backed by 0.5-inch lead sides and bottom. From the sink, the waste passes through a sediment trap before entering the soil line.

The trap is placed in a recess under the hood, where it is accessible for monitoring. The air is exhausted by a fan mounted in a chamber above the roof, so that a negative pressure exists in the duct inside the building leading to the roof. With this arrangement it is possible to monitor the exhaust as it is discharged above the top of the building. The air, flowing at 100 linear feet per minute through the aperture of the hood, is exhausted through an expansion chamber fitted with two folding cloth filters in series before entering the duct. The fan, operated by a time clock, runs automatically from 6 A.M. to 6 P.M. with a bypass switch to provide for after-hours operation.

Steam, air, and gas are available from hose nipples mounted within easy reach in the upper left-hand side of the hood, and are controlled by valves mounted on the front. A separate water outlet, also controlled externally, discharges into the sink. There are no apertures in the concrete framework lower than 3.5 feet above the working surface. Illumination is provided by two explosion-proof corner lights mounted inside the hood. Alternating and direct current outlets are mounted on the outside walls of the hood.

In case of spillage or spatter, the stainless steel deck can be removed for cleaning or for replacement. No removable panels were placed on the side walls, but the baffle which forms the back of the working chamber can be easily replaced. It would
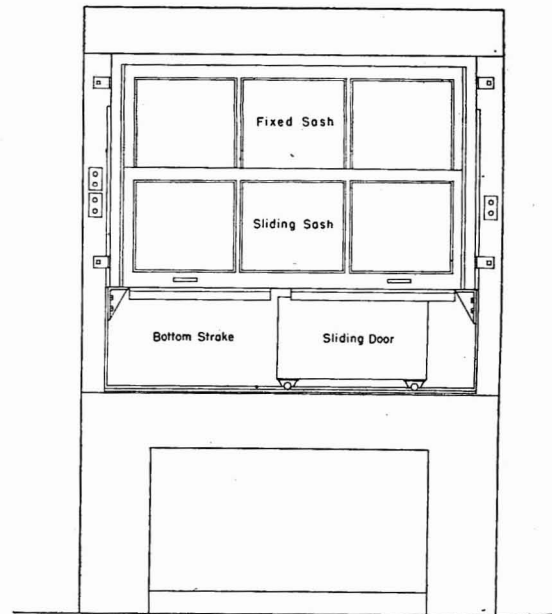

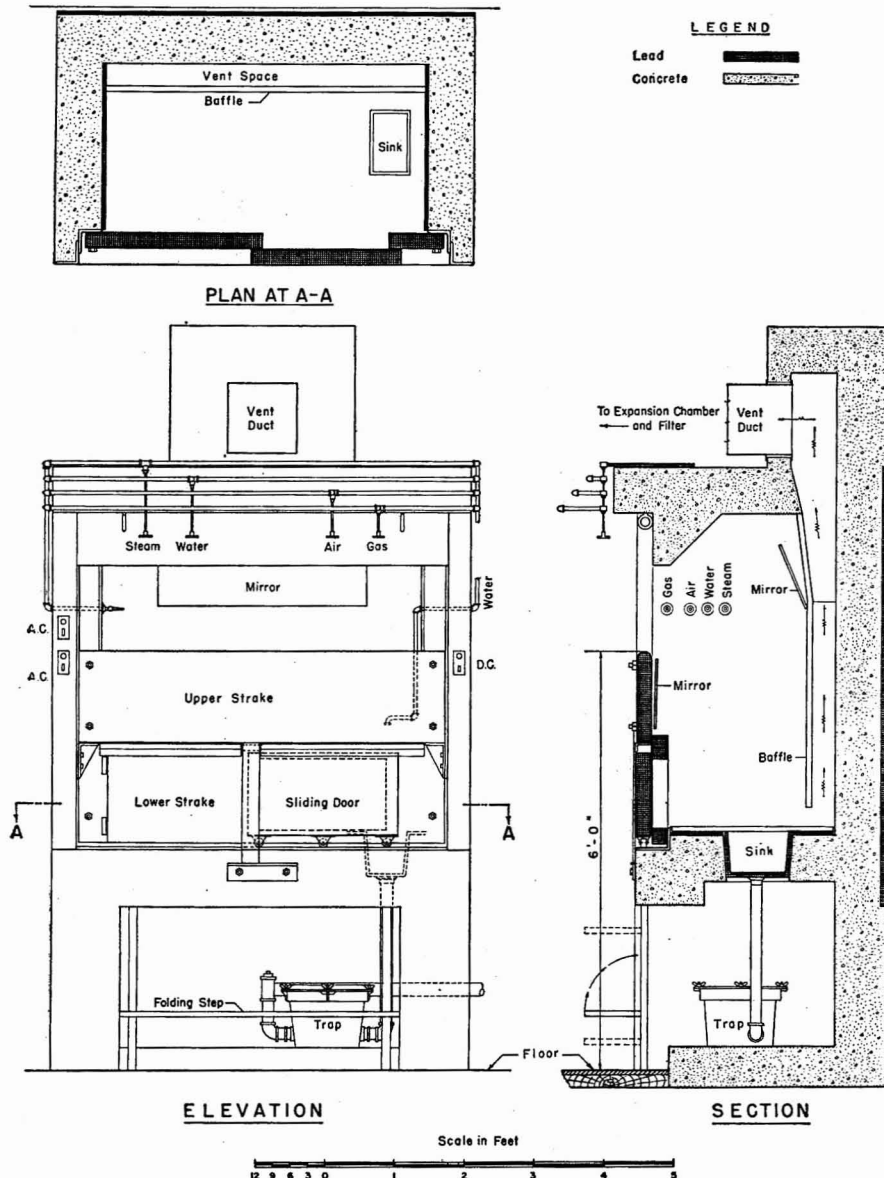Figure 2. Hood Modified for Moderate Sources of Radioactivity

seem advisable to include a removable facing on the side walls in future hoods of this type.

The working platform is 17 inches below the bottom of the sash. In practice this well has been found most convenient, because it provides protection for flasks on tripods over Bunsen burners, for material during distillation, and for radioactive substances that are centrifuged inside the hood. No inconvenience seems to have been introduced by working over this low barrier.

For the more intense sources, the front consists of two removable lead-filled steel strakes. An aperture in the bottom strake has an opening 22 inches wide by 12 inches high, which can be covered by a lead-filled steel door. The door, which rolls on steel rollers on a brass track, closes the aperture with an overlap of 2 inches. The upper strake, 15.75 inches high, has not yet been used in view of the small activity of the radioactive material so far. When in place, it leaves an aperture above it the full width of the hood and 15 inches high. An extension handle can be fitted onto the valves controlling the services so that, if necessary, they can be operated from a protected position below the top of the upper strake. It is possible to see into the hood through a two-mirror system, one mounted permanently inside the hood, and the second mounted removably on the inside of the upper strake. Thus, when it is necessary to work with indirect vision, the operator will not have the additional disadvantage of inverted images.

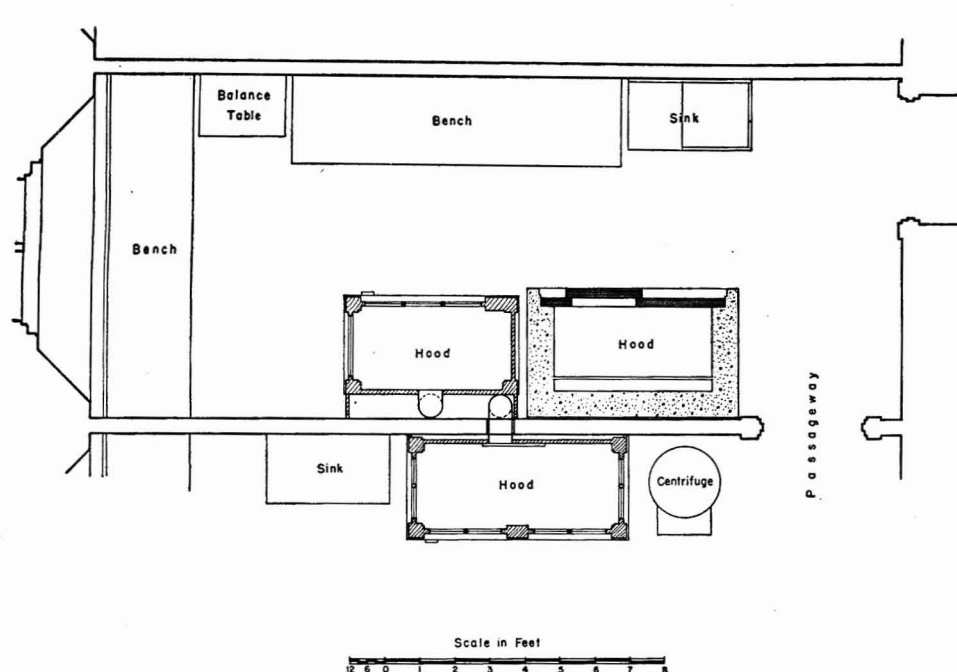Figure 1. Plan of Hood Designed for Intense Sources of Radioactivity

Figure 3. Plan of Laboratory, Showing Position of Hood and Inverse Square Law Shielding Available

Interior passageway used only for communication between two laboratories

When it became apparent that the upper strake would not normally be required, a vertical sliding sash was fitted to close the aperture. In order to handle intense sources, it is necessary only to remove the sliding sash and replace it with the upper strake. A convenient platform on which to stand is provided by a foldaway step, extending the full width of the hood and adjustable in height.

In case the shielding provided by the front steel and lead strakes is not sufficient, it is easily possible to build additional shielding inside the hood using lead bricks. Nuts welded into the inside surface of both strakes make possible the use of solid crossbars as stays for this additional shielding.

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CRYSTALLOGRAPHIC DATA

Contributed by Armour Research Foundation of Illinois Institute of Technology

THIS, the twelfth in the series of crystal descriptions, completes the first year of publication. Although only fifteen of the thousands of common and important compounds have been published, it is hoped that the data presented will be useful in themselves and as an aid in eventual complete structure determinations. It is further hoped that means can be found in the near future to increase the number of descriptions published each month.

During the past year several people have been kind enough to point out inconsistencies and errors in the published data. The major corrections required, however, are in the indexing of the powder lines. The principal errors include listing of reflections forbidden by the space group. Table I gives the correct index values for those compounds involved. The authors are grateful to I. Fankuchen for bringing these to their attention. They have also found, as a result of checking, that *a* and *c* are reversed in the description of *p*-aminoazobenzene. This does not, however, affect the other data, which were calculated with the correct *a* and *c*.
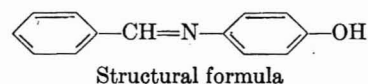
In future, index values will not be given for powder data because they are not in themselves analytical data and do not aid in cross checking other crystallographic data which are published in this series.

15. Benzalaminophenol

$$\langle\;\rangle-CH{=}N-\langle\;\rangle-OH$$

Structural formula

Benzalaminophenol crystallizes readily from alcohol, either by cooling or by dilution at room temperature with water. The crystals thus obtained are apparently identical with each other and with crystals obtained by sublimation or from fusion—no differences could be found microscopically, although powder diffraction data were slightly different for a sublimed sample and for crystals obtained by dilution of an alcohol solution (see below). The crystals used for x-ray diffraction were prepared by vacuum macrosublimation; the crystals for optical crystallography and morphology were recrystallized from alcohol.

Figure 1. *p*-Benzalaminophenol

Left. Crystals from sublimation on microscope slide
Right. Fusion preparation

Table I.   Indexing of Powder Lines (Corrected)

Adipic Acid		trans-Azobenzene		p-Methylaminophenol Sulfate		p-Aminoazobenzene		Thiamine Hydrochloride	
d	Index	d	Index	d	Index	d	Index	d	Index
6.82	001	7.03	002	9.33	200	9.05	101	7.79	...
4.67	$\bar{2}02, 20\bar{2}$	5.59	200	7.37	002	6.86	002	6.51	$\bar{1}11$
4.49	...	5.33	011	5.87	301, 010	5.25	202, 011, 110	5.80	200
4.13	011, 0$\bar{1}$1	5.12	110	5.60	110	4.97	$\bar{1}11$	5.42	021
3.79	...	4.88	...	5.44	011	4.56	202	4.86	221
3.52	200	4.62	00$\bar{3}$	4.66	400	4.31	210, 012	4.683	$\bar{1}11$
3.45	002	4.54	111	4.43	112	4.17	103	4.363	$\bar{1}21$
3.31	...	4.47	012	3.99	311, 402	4.02	112, 211	4.056	...
2.86	210	4.30	...	3.76	500, 013	3.55	400, 303	3.829	240
2.53	020	4.18	...	3.66	004, 303	3.28	$\bar{2}04$	3.403	212
2.51	201	4.02	210	3.48	204	2.93	204	3.201	002
2.41	120	3.82	...	3.37	...	2.79	020	3.122	012, 312
2.32	...	3.75	...	3.09	600	2.60	022, 220	2.889	400, $\bar{1}12$
2.26	00$\bar{3}$	3.67	202	2.92	020, 005	2.48	$\bar{2}22$	2.787	022, 420
2.19	...	3.51	004	2.81	220	2.44	...	2.684	042
2.14	...	3.39	...	2.74	221	2.39	$\bar{2}22$	2.559	360
2.10	220	3.29	...	2.67	206, 603	2.31	006	2.495	440
2.04	022	3.19	...	2.61	222	2.19	420	2.400	442
1.92	...	3.09	...	2.49	420	2.12	$\bar{5}05$	2.333	$\bar{2}22$
1.87	$\bar{2}02$	3.00	...	2.43	...	2.07	206	2.259	...
1.80	$\bar{2}22$	2.88	020	2.37	505, 422	2.01	224, 422	2.196	$\bar{2}42, 460$
1.76	400	2.80	005, 400	2.33	800	1.96	...	2.156	333, 462
1.71	004	2.68	022	2.28	024	1.87	505	2.106	003
1.50	222	2.57	220	2.25	224	1.79	$\bar{2}\cdot\cdot$	2.062	023
1.45	420	2.51	204	2.20	505, 224	1.76	606	2.015	550, 033
1.42	024	2.45	...	2.13	620	1.73	008, 033, 330	...	...
1.40	...	2.34	006	2.08	900, 424	1.63	408	...	...
1.28	040	2.27	222	2.03	424, 622	..	...	...	...
1.24	402	..	...	1.95	030, 130	..	...	...	...
1.22	240	..	...	1.88	026	..	...	...	...
..	...	..	...	1.84	033	..	...	...	...

Because the beta angle for p-methylaminophenol sulfate is almost 90° no effort has been made to differentiate between positive and negative h. All hk values for this compound then may be hkl.

CRYSTAL MORPHOLOGY (determined by W. C. McCrone).

Crystal System. Monoclinic

Form and Habit. The crystals prepared by sublimation are usually elongated parallel to a and show the clinopinacoid [010], basal pinacoid [001], and prism [110]. Crystals from alcohol may show additional dome forms and are usually not elongated. Axial Ratio. $a:b:c = 0.839:1:0.434$.

Interfacial Angles (Polar). 110 ∧ 1$\bar{1}$0 = 73°.

Beta Angle. 119½°; 118.6° (x-ray).

Twinning Plane. 100.

Color and Pleochroism. The crystals are a light yellow when pure and show slight pleochroism with strongest absorption along Z and least absorption along X.

X-RAY DIFFRACTION DATA (determined by J. F. Whitney and I. Corvin).

Cell Dimensions. $a = 12.54$; $b = 14.93$; $c = 6.48$.

Formula Weights per Cell. 4.

Formula Weight. 197.23.

Density. 1.303 (buoyancy); 1.25 (x-ray).

Principal Lines

d	I/I_1	d	I/I_1
8.74	0.09	2.805	unresolved 0.10
7.48	Very weak	2.75	
6.46(s)	0.10	2.703	
5.94	0.24	2.617	0.06
5.43(r)	Very weak, unresolved	2.435	0.19
5.25	0.73	2.376	0.09
4.85(r)	Very weak	2.255	Very weak
4.73(r)	Very weak	2.184	0.07
4.46	1.00	2.146	0.05
4.19(s)	0.66	2.100	0.07
4.06(s)	0.27	2.032	0.05
3.91	0.30	1.964	0.05
3.661	0.82	1.939	0.06
3.514	Very weak	1.894	0.07
3.333	Very weak	1.872	0.03
3.233	0.155(s), very weak(r)	1.821	0.03
3.152	0.38	1.779	0.02
3.076	0.42	1.752	0.04
2.886	0.10	1.731	0.03
		1.701	0.01
		1.672	0.02
		1.632	0.01

s, sublimed.
r, recrystallized from alcohol.
All lines except those noted are present in both sublimed and recrystallized samples.
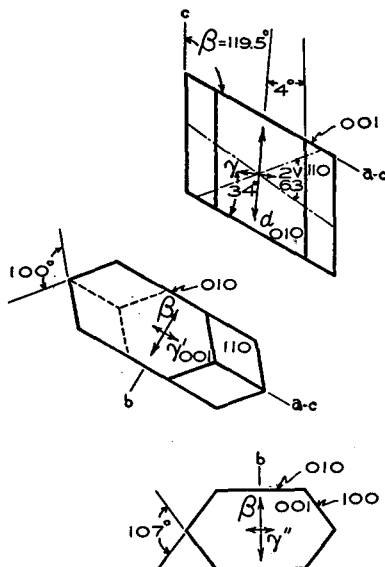

Figure 2.   Orthographic Projection of Typical Crystal of p-Benzalaminophenol

OPTICAL PROPERTIES (determined by W. C. McCrone).

Refractive Indices (5893 Å.; 25° C.). $\alpha = 1.698 \pm 0.002$. $\beta = 1.736 \pm 0.002$. $\gamma = 1.84 \pm 0.01$.

Optic Axial Angles (5893 Å.; 25° C.). $2V = 63°$.

Dispersion. $v > r$, very strong.

Optic Axial Plane. 010.

Sign of Double Refraction. Positive.

Acute Bisectrix. $\gamma \wedge a = 34°$ in obtuse beta.

Extinction. $\alpha \wedge c = 3°$ (blue); 5° (yellow) in obtuse beta.

Molecular Refraction (R) (5893 Å.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.756$. R(calcd.) $= 61.3$. R(obsd.) $= 62.1$.

FUSION DATA (determined by W. C. McCrone).

p-Benzalaminophenol melts at 183° C. without decomposition. If heated slowly, however, excellent crystals can be collected by sublimation on the underside of the cover glass. These crystals show 001, 010, and 110 and lie on 010 with a 60° profile angle or 001 with a 100° profile angle. The melt supercools readily but eventually solidifies spontaneously, albeit very slowly at room temperature. The crystal form is spherulitic at low temperatures; however, at higher temperature the crystals are larger and grow parallel over large areas.

A meltback gives rapid crystallization of broad rods, some crystals showing brilliant purple polarization colors indicating very high dispersion. The off-center optic axis interference figure shows a high 2E, very strong inclined dispersion, positive sign of double refraction, and BX_a outside the field. Some rods show oblique extinction and a flash figure.

Pittsburgh Analytical Symposium

THE Fourth Annual Pittsburgh Analytical Symposium, held January 20 and 21, was attended by almost 400 analytical chemists. Featured at the meeting was the general discussion by I. M. Kolthoff on the role of reaction kinetics in analytical chemistry. For the first time an instrument exhibit by eleven laboratory supply companies was held, featuring the newer analytical tools.

Role of Reaction Kinetics in Analytical Chemistry. I. M. KOLTHOFF, University of Minnesota, Minneapolis, Minn.

An understanding of reaction kinetics can be used in various analytical problems. A mixture of two compounds may contain two similar reactive (functional) groups which react in a similar way with a given reagent, but with different speeds. When the sum of both reactive groups is known, the amount of each constituent can be found from the amount of reagent that has reacted at a given constant temperature with a given excess of reagent after a suitable reaction period. The most favorable time of reaction can be derived from the rate constants of the two reactions of the functional groups with the reagent. Examples of this type of analysis are the determination of the amount of 1,2- and 1,4- addition in rubber by reaction with perbenzoic acid, the determination of two esters by saponification with base, and the determination of two compounds containing a carbonyl group by reaction with bisulfite or decomposition of the bisulfite addition products.

The accuracy of many oxidation reduction titrations can be greatly affected by the occurrence of induced reactions. Especially induced air oxidation can cause large errors. An understanding of the mechanism of such induced reactions can be applied to advantage for the improvement of analytical procedures. The reaction between dilute hydrogen peroxide and ferrous iron was discussed in detail in the presence and absence of organic compounds and of oxygen. An interpretation of the induced reactions was given. The results are used in the determination of traces of organic hydroperoxides in various organic materials by the ferrous iron method. Without considering the induced air oxidation this method may give errors of the order of 300 to 400%.

Statistical Methods in the Chemical Industry. A Case History. B. L. CLARKE, Merck & Co., Inc., Rahway, N. J.

The primary purpose of this paper was to interest those dealing with chemical processes who are not now making use of modern statistical methods in the statistical field. The thesis was presented and maintained that statistical methods hitherto used almost exclusively by nonchemical workers have inherently many logical adaptations to the chemical field.

The paper consisted essentially of the case history of a successful attempt to introduce statistical methods into a company manufacturing chemicals:

1. Type of problems statistics can be of help in
2. Where such problems arise in the chemical industry
3. What one company is doing toward solving such problems by statistical means
4. Future of this project
5. Generalized implications

Purity Determinations as Ascertained by Phase Studies. W. J. MADER AND H. A. FREDIANI, Merck & Co., Inc., Rahway, N. J.

The analyst is being called upon daily to determine the purity of compounds accurately. With the advent of the newer highly active pharmacological preparations where a small amount of closely related impurity may modify the drug entirely, it is necessary to have available a means of proving the compound's purity. This is of fundamental importance.

Ultimate analysis, boiling point, molecular weight, absorption, group analysis, etc., fail when one is dealing with isomeric compounds. Solubility analysis offers a means of analyzing such closely related organic compounds providing the other components are present as distinct phases, and the contaminants are present in substantial quantities (0.1% or better).

Solubility analysis has been used with considerable success on the following types of problems.

1. Establishing the purity of amino acids. The Merck specifications for amino acids state that they must contain 99% of the labeled compound—for example, dl-phenylalanine must contain not more than 1% of l-phenylalanine together with the other amino acids and impurities. Solubility analysis is one of the few means that can establish such a purity for these compounds.

2. Determining the number and quantities of impurities. The ortho, meta, and para isomers formed in the nitration of benzene to dinitrobenzene have been determined.

3. Determination of the purity of many compounds such as paracodine tartrate, arabinose, sorbose, and sulfaquinoxaline.

The technique involved is fairly simple, though tedious. One prepares a series of suspensions of the compound in a suitable solvent, equilibrates the solutions by tumbling in a constant temperature bath, removes some of the supernatant liquid, and determines the amount in solution. If each suspension has identical solubility, the compound is pure; if not, the increase in solubility is an indication of the amount of impurity present.

Electrolytic Separation of Rhodium from Iridium at a Controlled Cathode Potential. WILLIAM MARSHALL MacNEVIN AND SAMUEL MILLER TUTHILL, Ohio State University, Columbus, Ohio.

The electrolytic separation of rhodium from iridium has been successfully accomplished using a controlled cathode potential circuit of the Lingane type. The solution contained 3.5 molar ammonium chloride and the cathode was operated at 0.4 volt more negative than the saturated calomel electrode. Rhodium deposits were found to contain oxide and it was necessary to reduce the electrolytic deposit in hydrogen gas at 450° C. Iridium, although it does not deposit at voltages up to 1.0 volt more negative than the saturated calomel electrode, codeposits strongly at −0.3 volt (vs. S.C.E.) in the presence of rhodium. The cause of this induced codeposition of iridium has not been explained but it has been prevented by preliminary destruction of complex ions, oxidation of iridium to the tetravalent state before electrolysis and by the addition of sufficient ammonium chloride (3.5 M). The adaptation of the electrolytic separation to the Gilchrist-Wichers scheme for the platinum group metals was discussed.

Polarographic Technique in Organic Analysis. PHILIP J. ELVING, Purdue University, Lafayette, Ind.

The basic principles of polarographic measurements as applied to organic compounds were reviewed. From such measurements it is possible to determine organic compounds and functional groups quantitatively with a precision of 1 to 4 parts per hundred. The factors to be considered in developing and applying polarographic methods of analysis to organic compounds were discussed. Under favorable conditions, mixtures of such closely related compounds as isomers can be analyzed. Many organic compounds which are not polarographically electroreducible or electro-oxidizable can be converted to polarographically measurable compounds by simple quantitative reactions. In addition to strictly analytical uses, applications of the polarographic technique include the determination of reaction rates, the elucidation of reaction mechanisms, the study of keto-enol equilibria and of cis-trans isomeric compounds, the behavior and extent of hydrogen bonding, and the measurement of relative redox potentials.

Analysis of Molybdenum-Tungsten and Cobalt-Molybdenum-Tungsten High Speed Steels. WALDO L. EMERSON, The Cleveland Twist Drill Co., Cleveland, Ohio.

This paper outlined the procedures used in the laboratory of the Cleveland Twist Drill Company for the sampling and analysis of molybdenum-tungsten and cobalt-molybdenum-tungsten high speed steels for the elements carbon, manganese, silicon, chromium, tungsten, vanadium, molybdenum, and cobalt.

Detailed outlines of colorimetric procedures for manganese, molybdenum, and tungsten were given. None of the methods is new but certain critical steps were emphasized and expected accuracies by the procedures employed were noted.

A procedure for the precipitation of cobalt by α-nitroso-β-naphthol, which results in an easily filterable solution, was outlined.

Attention was given to the polarographic determination of residual copper, nickel, and cobalt, employing a slight modification of the method of Lingane and Kerlinger.

Determination of Nitrogen in Steel. JOHN L. HAGUE, National Bureau of Standards, Washington, D. C.

A rapid titration method was described for the determination of nitrogen in steel. A sample weight of 0.5 to 1.0 gram is usually

required, and the nitrogen is put into solution as ammonium sulfate by appropriate treatment of the sample with sulfuric acid. The ammonia formed in the process is separated from the bulk of the sample by steam distillation from an alkaline solution. The distillate is collected in boric acid solution, and the nitrogen is determined by titration with 0.01 N acid. Provision is made for the solution of difficultly soluble nitrides, and the effect of some of the commonly used alloying elements on the solubility of nitrogen compounds in steel was discussed. An accuracy of the order of 0.002% nitrogen is indicated for samples containing up to about 0.10% nitrogen. In the lower range of nitrogen contents, somewhat better accuracy can be obtained by attention to pertinent details. A single determination can be completed in less than 10 minutes after solution of the sample, and a group of ten determinations can be carried out in approximately 2 hours.

Ultraviolet Absorption Analysis for Naphthalenes. NORMAN D. COGGESHALL AND ALVIN S. GLESSNER, JR., Gulf Research & Development Co., Pittsburgh, Pa.

A method for the analysis of hydrocarbon mixtures boiling in the kerosene range for naphthalene, α-methylnaphthalene, and β-methylnaphthalene is based on the ultraviolet absorption characteristics of the naphthalenes. Despite the rather close similarity of the spectra of these compounds it has been found practical to analyze for all three at the same time using the usual method, based on Beer's law of absorption, wherein data taken at several different wave lengths are used. The accuracy obtainable under routine conditions is satisfactory, the average errors being less than 0.3% of the total sample. This was tested using synthetic samples and by making material balance calculations on the data obtained from several distillation and concentration processes. For proper utilization, the cuts must be made between definite temperature limits. In a number of cases it is desirable to determine the naphthalene content of lower boiling cuts which do not contain methylnaphthalenes, but do contain large concentrations of mononuclear aromatics. These latter compounds, by virtue of their heavy concentrations, contribute appreciable "background" absorption at the characteristic absorption wave lengths of naphthalene. To determine the naphthalene content it is necessary to determine the amount of background contribution and to correct suitably for it, by utilizing numerical relationships between various points in the naphthalene spectrum. The accuracy of the method is satisfactory, the average errors for samples containing up to 10% naphthalene being no larger than 0.1% total sample. This was tested by means of synthetic samples and by re-examining actual samples to which known amounts of naphthalene had been added.

Some Operational Experiences with Infrared Gas Analyzers. WILLIAM J. HAPPEL AND NORMAN D. COGGESHALL, Gulf Research & Development Co., Pittsburgh, Pa.

The development within the past few years of instruments based on selective infrared absorption which give a continuous record of the concentration of one component in a product gas stream is of material aid in process investigations. This paper outlined and briefly described some of the operational experiences encountered in the applications of such an analyzer to pilot plant operation.

As it is sometimes necessary that the instruments utilized in pilot plant operation be serviced by nontechnical personnel, it is of very great importance that their operation and maintenance be as simple as possible and their performance be consistently reliable. In achieving these conditions it was found necessary to make a number of instrument modifications. A sensitivity or scale expander circuit was installed. This allows an electrical compensation to be made for any loss of sensitivity due to changes in the optical part of the equipment and it also permits the sensitivity to be adjusted to any desired value. An additional regulation, provided for the radiation source, was done through the use of neon lamps and resulted in less drift and greater base line stability. The use of the instruments for streams containing sulfur dioxide led to a chemical deterioration of the cement retaining the cell windows. It was necessary to develop a technique for the cementing of windows which would not be affected by such gases. In some cases there were very large variations in the concentration of water vapor in the stream. Previously, all the water vapor had been removed by use of a drying train. It was found advantageous to investigate those cases in which the water vapor would not affect the results or corrode the system and permit wet gas to pass through when possible. Details of such tests were given.

Spectrum Excitation with the Use of the Quantometer. J. R. CHURCHILL, Aluminum Research Laboratories, New Kensington, Pa.

The use of the Quantometer in the development of methods for the analysis of aluminum has provided valuable information on various factors influencing excitation. The effects produced by surrounding the analytical gap with air, nitrogen, argon, and helium were described and the influence of water concentration in various atmospheres was discussed. Results of preliminary investigations on the influence of matrix variations and metallurgical history of samples were given.

Experiences in the Quantitative Spectrographic Analysis of Brines. R. G. RUSSELL, Gulf Research & Development Co., Pittsburgh, Pa.

Brines are not the type of samples that can be easily analyzed using spectrographic methods. It was the desire to develop a spectrographic method which would be more rapid than conventional chemical procedures as well as give information not ordinarily obtained by such methods. The net result was a quantitative spectrographic procedure for nine elements in brine which is not ideal because of hygroscopicity of the brine samples but which gives acceptable results for these nine elements.

An alternating current spark method on briquetted pellets is employed and details were given. Standards can be prepared for elements capable of being determined spectrographically and an over-all precision of ±10% of the elements can be obtained. A method for the determination of the major constituents (sodium, magnesium, calcium) was explained.

The Doubling Factor Applied to Emulsion Calibration Curves and Working Curves. E. M. McMAHAN, Aluminum Research Laboratories, New Kensington, Pa.

Two concepts, "doubling ratio" and "doubling length," have been introduced to describe emulsion calibration and working curves. The doubling ratio is the ratio of the intensities corresponding to a doubling of the ordinate value. The doubling length is the distance spanned by these intensity values—i.e., the logarithm of the doubling ratio. The convenience of these concepts was illustrated by using them to construct curves, to perform certain calculations useful in making comparisons between curves, and also to develop an equation showing the magnitude of the error arising from the use of an incorrect calibration curve.

Comparative Study of Methods for the Determination of Nickel. M. D. COOPER, General Motors Corp., Detroit, Mich.

The paper presented a comparison of the gravimetric, spectrophotometric, polarographic, and cyanide titration methods for the determination of nickel in steel. The methods were compared with respect to their reliability and speed, the former based on maximum and standard deviation data and the latter on the time required to analyze a large number of samples simultaneously. For the comparative study four samples were chosen which provided nickel values ranging from 0.04 to 2.0%.

The investigation of the polarographic method was limited to a study at one nickel level because of unavailability of an adequate supply of a particular reagent of suitable purity. Further progress with the method will depend upon solving the problem of reagent supply. The paper presented the limited data obtained and defined the difference between suitable and unsuitable reagent from the performance standpoint.

In regard to the spectrophotometric method a new approach in the oxidation of nickel to obtain the soluble dimethylglyoxime compound was described. The effect of copper and manganese on the absorbency of solutions of the nickel compound and the errors which may attend disregard of the interference of these elements constituted a major phase of the discussion. In addition to the material related to the analysis of steel, the method was shown to be applicable in the analysis of aluminum alloys. In the latter a modified procedure, which permits the accurate determination of nickel in the presence of copper, was shown to be twice as rapid as methods which depend upon preliminary removal of copper.

An Improved Method for the Determination of Phosphorus in Alloys. JAMES L. KASSNER AND MARY ALICE OZIER, University of Alabama, University, Ala.

The determination of phosphorus in cast iron, steel, and other alloys is carried out in three steps—solution of the sample, pre-

cipitation of the ammonium molybdiphosphate, and titration of this salt to determine the amount of phosphorus present. This study dealt specifically with the second and third steps in this procedure. The solution of the samples is effected in each case by standard procedure.

This study shows that the time for a complete determination can be shortened by using a double-strength citromolybdate solution in place of the conventional ammonium molybdate solution and separating the ammonium molybdiphosphate precipitate at the boiling point. The nitric acid-free precipitate is dissolved in an excess of standard solution of sodium hydroxide, and the excess caustic is titrated with standard nitric acid in the presence of the new mixed indicator used in the determination of phosphorus pentoxide in phosphate rock. The analysis of twenty Bureau of Standard samples indicates that the accuracy and precision of this method are good.

Separation of Cesium from the Other Alkalies, and the Preparation of Cesium Bromide. V. A. STENGER, The Dow Chemical Co., Midland, Mich.

In a study of the solubilities of various metal halides in liquid bromine, it was found that cesium bromide is very soluble whereas the bromides of other alkali and alkaline earth metals are not. This solubility difference has been utilized for the separation of cesium from other elements and has been applied on a pilot plant scale for the production of cesium bromide from pollucite ore. Pollucite, a cesium aluminum silicate, is leached with hydrobromic acid, leaving silica as a residue. Alkali bromides are precipitated with isopropanol, in which aluminum bromide is soluble. The precipitate is rinsed with isopropanol, then is dried and extracted with bromine. Evaporation of bromine from the extract leaves cesium bromide, which is easily purified by crystallization from water.

Cesium bromide is suggested as a convenient starting material for the preparation of other cesium salts, particularly for use as analytical reagents.

Isoquinoline as a Reagent in Inorganic Analysis. Zinc. A. E. SPAKOWSKI AND H. FREISER, University of Pittsburgh, Pittsburgh, Pa.

Isoquinoline, a tar base recently made commercially available, has many properties desirable in an analytical reagent. When a

solution of isoquinoline and a thiocyanate is added to solutions of certain divalent cations, precipitates corresponding to the formula $Me(C_9H_7N)_2(CNS)_2$ are formed. The general nature of the reaction was considered. The reagent, already successfully applied to the analysis of copper in alloys and ores, also provides a means for the gravimetric determination of zinc, since the precipitates of the two cations are formed at different pH's. The average accuracy of the method applied to the estimation of zinc in brasses is 3 to 4 parts per thousand.

Umpire Method for the Determination of Tin in Plain Carbon Steel. W. R. SAYRE AND G. NORMAN REIS, Edgar Thompson Works, Carnegie-Illinois Steel Corp., Braddock, Pa.

This paper reports a study of some features of the umpire method. This old, familiar method is more attractive than it appears at first glance. The following alterations to the original method are proposed: The use of ammonium sulfide instead of hydrogen sulfide. The use of potassium thiocyanate to indicate the proper condition for complete precipitation of the tin. A simplified reduction and titration procedure.

Plain carbon steels, which yield stable organic tin compounds were discussed.

A procedure for determining tin in plain carbon steels with an accuracy of about ±0.0005% was outlined.

Vacuum Fusion Gas Analysis of Metals, Particularly Steel. W. A. PEIFER, Allegheny Ludlum Steel Corp., Brackenridge, Pa.

An introductory explanation of the nature of vacuum fusion analysis and the reactions involved was given. Various designs of vacuum fusion analysis equipment were described and their merits discussed. The operation procedure for a typical apparatus was described. The method of making the so-called fractional vacuum fusion analysis was described with a brief discussion of the nature and usefulness of the results so obtained. Procedures for sampling and for preparation of samples were discussed with emphasis placed on precautions, particularly in reference to samples which are to be analyzed for hydrogen. Precision and accuracy obtainable with present equipment were indicated. The usefulness of this method of analysis was indicated by examples of problems successfully elucidated by its use.

Philadelphia Meeting-in-Miniature

THE Third Meeting-in-Miniature sponsored by the Philadelphia Section, AMERICAN CHEMICAL SOCIETY, was held in Philadelphia, January 20, 1949. Papers of special interest to analytical chemists are abstracted here.

A Thermometric Method for the Determination of Sulfur Trioxide in Chlorosulfonic Acid. W. SEAMAN, J. T. WOODS, AND M. N. BANK, Calco Chemical Divison, American Cyanamid Co., Bound Brook, N. J.

A more precise and specific method was needed for the determination of sulfur trioxide in chlorosulfonic acid than the conventional procedure involving the determination of total acidity and chloride values from which the sulfur trioxide may be calculated indirectly. This need was met by a method that involves measuring the temperature rise which occurs when dry hydrogen chloride, passing through the sample, reacts with the sulfur trioxide and calculating the sulfur trioxide content of the sample from a standard equation.

Over the range 0.4 to 2.8% sulfur trioxide the method has a precision expressed as a standard deviation of ±0.024% (absolute) of sulfur trioxide. There is no reason to believe that there is any systematic error. Sulfuric acid does not interfere, at least in concentrations up to 5%.

For the conditions described 3% sulfur trioxide is the upper limit of the concentration of sulfur trioxide that may be determined by the method, but samples containing as much as 35% sulfur trioxide have been measured by dilution techniques with a precision somewhat better than may be attained by the usual procedure involving the determination of the total acidity and chloride values.

There is some evidence for the existence of the equilibrium:

$$ClSO_3H \rightleftharpoons SO_3 + HCl$$
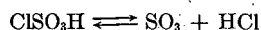
Volumetric Determination of Small Amounts of Iron. Chromous Chloride as Reducing Agent. W. D. COOKE, F. HAZEL, AND W. M. McNABB, University of Pennsylvania, Philadelphia, Pa.

A method was described for the volumetric determination of iron in samples ranging from 0.1 to 9 mg. of iron. The accuracy of the method is 0.2 to 1%, depending upon the weight of the sample. The time required for a complete analysis is 2 to 3 minutes.

Chromous chloride solution is used to reduce ferric iron to the ferrous state. The excess chromous ion is oxidized by atmospheric oxygen. No appreciable oxidation of the iron occurs under the conditions of the experiment. The ferrous iron is titrated with a standard dichromate solution using diphenylamine sulfonate as indicator. The chromous chloride solution is stored in an ordinary dropping bottle with a small amount of liquid zinc amalgam which keeps it reduced.

Five to 25 ml. of ferric iron solution containing 0.1 to 9 mg. of iron are acidified with either sulfuric or hydrochloric acid. One or 2 drops of phenosafranine indicator are added. To this are added one or two drops of a chromous chloride solution until the pink color of the indicator disappears and the solution becomes a light, clear-green color. The solution is swirled until the pink color reappears. A few drops of 50% phosphoric acid and 0.05 to 0.1 ml. of diphenylamine sulfonate are added and the ferrous iron is titrated with a 0.007 or 0.003 N solution of potassium dichromate. The end point is reached when the color of the solution changes from a light pink or violet to a purple color.

Determination of Glucose, Galactose, and Rhamnose in Mixtures. W. L. PORTER AND C. S. FENSKE, Jr., Eastern Regional Research Laboratory, Philadelphia, Pa.

A method was presented for the analysis of all possible combinations of glucose, galactose, and rhamnose as encountered in hydrolyzates of flavonol glycosides. The sugar determinations are made by Schrool's copper reduction method, before and after

fermentation by *Saccharomyces bayanus* (N.R.R.L. No. 966) and *Saccharomyces carlsbergensis* (N.R.R.L. No. 379), which are capable of the selective destruction of glucose and of glucose and galactose, respectively. To minimize the amount of fermentation and quantitative analytical work necessary, filter paper chromatography is employed for the qualitative analysis of the sugars present.

Determination of Unsaturation by Microhydrogenation. Method and Apparatus. C. L. OGG AND F. J. COOPER, Eastern Regional Research Laboratory, Philadelphia, Pa.

A new hydrogenation microapparatus which is simple in its construction and easily operated, was described. The apparatus consists of a reaction unit attached to the buret-manometer assembly of a Soltys active hydrogen apparatus. During hydrogenation, the reaction mixture is agitated by a magnetic stirrer. The preparation of the palladium on a carbon catalyst and the method of determining unsaturation in organic compounds by hydrogenation were given.

In many compounds, unsaturation can be determined with much greater accuracy by microhydrogenation than by macrohalogenation methods. Results of the analyses of some monounsaturated acids and of some conjugated and nonconjugated polyunsaturated acids and their esters were given.

KARL FISCHER REAGENT. C. RICCIUTI AND C. O. WILLITS, Eastern Regional Research Laboratory, Philadelphia, Pa.

A survey has been made of literature references to the Karl Fischer reagent, and all formulas have been put on a common basis. By expressing the molar concentrations of the different components, a means of comparison of the reagents has been developed.

A rapid and simple method of standardization of Karl Fischer reagent was given:

To the reaction vessel a few milliliters of Karl Fischer reagent usually 5 ml., are added to provide anhydrous conditions. The excess reagent is destroyed by addition of the standard water-methanol solution.

A second portion of Karl Fischer reagent, usually 10 ml., accurately measured to the nearest 0.01 ml., is added and titrated with the standard water-methanol solution. From the volume of standard water-methanol solution and the volume of Karl Fischer reagent, the ratio of standard water-methanol solution to reagent is found.

A quantity of the reagent methanol is added and a known volume of Karl Fischer reagent, in excess of the water in the added reagent methanol, is added. This mixture is back-titrated with standard water-methanol solution. By means of the following equation, the titer of the reagent can be calculated.

$$\frac{WQM}{Q + P - MR} = \text{mg. of } H_2O \text{ per 1 ml. of Karl Fischer reagent}$$

$M = \dfrac{\text{volume of standard water-methanol solution}}{\text{volume of Karl Fischer reagent}}$

W = weight of added water, mg. per ml. of water-methanol solution

Q = volume of reagent methanol

R = volume of Karl Fischer reagent

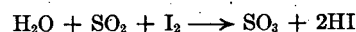P = volume standard water-methanol solution

This method provides a convenient means of standardization of the Karl Fischer reagent and avoids the preparation of absolutely anhydrous methanol or the errors inherent in the weighing of small amounts, 100 to 200 mg. of water.

Stoichiometric Iodometric Method for Determination of Water by Karl Fischer Reagent. W. SEAMAN, W. H. McCOMAS, JR., AND G. A. ALLEN, Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J.

The Karl Fischer reagent for the determination of water, which consists of a solution of iodine in sulfur dioxide, pyridine, and methanol, suffers from two shortcomings: It rapidly undergoes considerable decomposition, thus requiring frequent restandardization; and it must be standardized empirically against water and cannot be used on the basis of its iodine content.

A modified Fischer technique was proposed. The reagent is made up and used in the form of two solutions—one containing sulfur dioxide, pyridine, and methanol (for dissolution or dispersion of the sample) and the other containing iodine and methanol (for titration of the water). The water content of a

sample is calculated from the iodine contained in the volume of the second solution consumed, according to the equation:

$$H_2O + SO_2 + I_2 \longrightarrow SO_3 + 2HI$$

The iodine solution is standardized with thiosulfate, but its water content must also be taken into account. It is stable if protected from the absorption of atmospheric moisture.

Determination of water in a number of samples by both the usual method and the proposed method indicated satisfactory agreement. Conditions were described under which water may be determined, if necessary, in the presence of excess reagent followed by back-titration with water, with a minimum of decomposition.

End Point in Arsenite Titration of Chlorine. E. L. ECKFELDT AND W. E. PROCTOR, Leeds & Northrup, Philadelphia, Pa.

The arsenite titration of free available chlorine in concentrations of the order of 1 mg. per liter possesses certain advantages over other methods. The end point of this reaction was studied by an amperometric and a potentiometric method to estimate the possible accuracy of the determination. The amperometric method is similar to that described by Marks and Glass [*J. Am. Water Works Assoc.*, **34**, 1227 (1942)], but employs a simplified apparatus readily assembled from standard laboratory equipment. The potentiometric method employs a pH meter, with voltage scale, and standard types of electrodes. Because potentiometric readings in the region of this end point tend to be unreliable, a method of extrapolation was proposed which uses the more reliable points immediately preceding the end point. The results obtained by both methods were compared, and conclusions were drawn.

High Temperature Combustion Technique for Determination of Fluorine. O. I. MILNER, Socony-Vacuum Research Laboratories, Paulsboro, N. J.

Fluorine, in highly fluorinated hydrocarbons and oxygenated organic compounds, is usually determined by lengthy and tedious methods involving decomposition of sample with metallic sodium or potassium in a nickel bomb at a temperature of 400° to 500° C. In the procedure described the sample is completely burned at 1250° C. in an atmosphere of oxygen and water vapor, utilizing a platinum combustion tube. The fluorine is liberated as hydrogen fluoride, which is estimated by alkalimetric titration. Partially or completely fluorinated materials, in either liquid or solid state, may be analyzed by this method. Carbon, in the presence of fluorine, is very difficult to determine by conventional combustion methods; it may, however, be readily estimated by this method. Advantages of this technique are precision and rapidity. Fluorine contents, in the range of 75 to 80%, may be determined with an accuracy of ±1%. A single determination may be completed in 2 hours as compared to an over-all time of 12 to 18 hours for the bomb decomposition procedure.

Polarographic Determination of Lead in Organic Compounds. J. R. GLASS, Socony-Vacuum Research Laboratories, Paulsboro, N. J.

Lead in new and used oils and organic preparations is generally determined by a lengthy gravimetric procedure involving reduction of the sample to ash, solution of latter in appropriate solvent, removal of interfering elements, with subsequent precipitation, and isolation of lead as chromate or sulfate. In the polarographic procedure described, the sample is rapidly decomposed by wet oxidation in a Kjeldahl flask with a minimum amount of hot concentrated sulfuric acid and 30% hydrogen peroxide solution. After neutralization of residual sulfuric acid with alkali and conversion of the resulting lead sulfate with excess sodium hydroxide to the soluble, polarographically active plumbite ion a well-defined polarogram is recorded at 0.75 volt on the solution, using gelatin as a maxima suppressor. Concentration of the lead in the sample is readily determined by comparing the polarogram with one obtained on a standard solution of lead. Advantages of the procedure are rapidity, precision, and almost complete freedom of interference from other elements. In general, the precision that may be expected is in the order of ±1%.

A Colorimetric Determination of Piperonyl Butoxide in Presence of Pyrethrins. J. C. DAVIDSON AND H. D. TERRELL, Refinery Technology Division, Gulf Oil Corp., Philadelphia, Pa.

A tentative colorimetric method for the determination of piperonyl butoxide in odorless base oil has been developed by the Howard A. Jones Applied Research Laboratories and distributed

by U. S. Industrial Chemicals, Inc. This method is satisfactory if pyrethrins are not present in appreciable concentrations. However, as the concentration of pyrethrins is increased, the background absorbence is increased and the absorbence due to the piperonyl butoxide is decreased.

A modification of this method, in which this interference is largely overcome, involves removal of the pyrethrins by a 5-hour hot saponification with 1 N alcoholic sodium hydroxide. Three standard solutions of 0.10, 0.20, and 0.30% by volume piperonyl butoxide in odorless base oil and a blank solution of base oil are saponified in the same manner. The oil layers are washed with water and filtered through filter paper until clear, 0.2 ml. of each solution is placed in test tubes, and 5 ml. of a coloring reagent consisting of 0.1 gram of tannic acid, 30 ml. of glacial acetic acid, and 70 ml. of 85% phosphoric acid are added to each. The tubes are shaken simultaneously for 3 minutes and then simultaneously immersed in a vigorously boiling water bath for 5 minutes. A blue color is developed which is measured on a photoelectric colorimeter.

The absorbences of the standards when plotted against concentration of piperonyl butoxide form a straight line which follows Beer's law.

Analysis of Mixtures of Amines by Reaction of Carbon Disulfide. E. L. STANLEY AND R. V. SAVACOOL, Rohm and Haas Co., Philadelphia, Pa.

In 1868, A. W. Hoffman observed that a mixture of carbon disulfide, ethylamine, and silver nitrate reacted to form a white precipitate of "Aethylsulfocarbaminsäure Silber" and the nitric acid salt of ethylamine; and that the silver salt gradually decomposed to silver sulfide and ethylisothiocyanate. There is no evidence that this reaction has been used for quantitative determination of aliphatic amines. In 1913, H. S. Fry employed carbon disulfide in the determination of aniline according to the reaction

$$RNH_2 + CS_2 + I_2 + 2C_5H_5N \longrightarrow RNCS + 2C_5H_5N \cdot HI + S$$
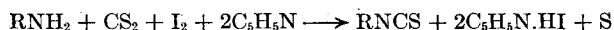
Two new methods were developed, both based on the fact that carbon disulfide reacts with mono- and dimethylamine, but not with trimethylamine, to form the corresponding dithiocarbamates. These may be determined either by a rapid titration with silver nitrate solution, which is only semiquantitative; or by a longer, but highly accurate method in which the dithiocarbamate is decomposed with acid, the resulting carbon disulfide purified by passage through a lead acetate scrubber, and trapped by reaction with alcoholic potash to form a xanthate, which is titrated with standard iodine solution. The method of Fry has been applied to octadecyl amines.

Modified Pettenkofer Reaction Applied to Determination of Dehydroisoandrosterone in Pure Solution and in Urine Extracts. L. HANSEN, Jefferson Medical College, Philadelphia, Pa.

Kerr and Hoehn (1944) showed that a modified Pettenkofer reaction produced a color which was qualitatively positive for very few of a variety of steroids tested. Among those giving a positive test was dehydroisoandrosterone and it was suggested that this method might be an approach for the quantitative determination of this steroid.

Initially the method of Kerr and Hoen was applied to available steroids on a quantitative basis, but later modifications were tried with the object of increasing and stabilizing the color, producing a color conforming more satisfactorily to Beer's law, and simplifying the technique as regards apparatus, reagents, and time.

The absorption curve for dehydroisoandrosterone was determined spectrophotometrically with a Beckmann spectrophotometer over the range 325 to 900 millimicrons, giving maxima at 655 and 375 millimicrons. With the Evelyn photoelectric colorimeter Rubicon filter 660 was found most favorable and was employed for all comparative and quantitative tests.

A number of types of steroids, including cholesterol and a series of bile acids, were compared in 100-microgram aliquots. Some were also tested with larger aliquots. Positive colors were obtained comparable to the color with dehydroisoandrosterone with cholic acid, dehydroisoandrosterone, androstenediol, pregnenolone, and isoandrosterone. Comparison of results obtained with various related steroids suggests structural features of steroids for positive color reaction.

Admixtures of androsterone and dehydroisoandrosterone in varying proportions indicate absence of effect of androsterone on the color obtained with dehydroisoandrosterone.

Quantitative estimation of dehydroisoandrosterone in pure solution, urine extracts, and with added hydroisoandrosterone to such extracts was obtained and compared with determination by other methods.

Application of McCarthy-Sullivan Procedure for Determination of Methionine to Various Thio Ethers. K. WEISS AND J. A. STEKOL, Lankenau Hospital Research Institute, Philadelphia, Pa.

In connection with the study of the biochemistry of thio ethers, quantitative determination of methionine in biological materials containing the thio ethers became desirable. Before applying the McCarthy-Sullivan procedure for the determination of methionine to such materials it appeared desirable to test the specificity of the reaction using various homologs, analogs, and substitution products of methionine. Sixteen such compounds were synthesized and the McCarthy-Sullivan procedure was applied to them. Cystathionine, methionine sulfoxide, S-β-carboxyethylcysteine, and homocystine gave no color at all concentrations employed. On the other hand, biethionine, ethionine, S-n-propylhomocysteine, S-isopropylhomocysteine, bimethionine, N-benzoylmethionine, S-benzylhomocysteine, S-carboxymethylhomocysteine, and S-β-carboxyethylhomocysteine gave color in intensities of 12 to over 200% of that given by methionine calculated on molar basis.

Speculations could be made in regard to the influence of certain groupings on the color development in this procedure. The application of the McCarthy-Sullivan reaction for the determination of methionine in biological materials whenever any of the above thio ethers, with some exceptions, are used is of questionable value.

Microdetermination of Calcium and Magnesium in Animal Tissues. J. J. KOLB AND G. TOENNIES, Lankenau Hospital Research Institute, Philadelphia, Pa.

The method for calcium is based on that of Sendroy for blood serum. Several modifications had to be introduced to adapt it to the analysis of tissue. The tissue is ashed at 450°, and the ash is dissolved in 1 ml. of 2 N hydrochloric acid and diluted. The calcium is precipitated at pH 6 as the oxalate and determined indirectly by oxidation of the oxalate with excess ceric sulfate. The excess oxidant is estimated spectrophotometrically (Coleman Model 11) by iodine liberation. Kolb and Toennies determined 6 to 20 micrograms of calcium with a mean deviation of approximately 5% from the average of triplicate analyses. The accuracy at the lowest levels, corresponding to approximately 40 mg. of fresh tissue, is within 10% of the theoretical.

The procedure is valid in the presence of an equal amount of magnesium and about 8 times as much phosphorus on a molar basis. The pH at precipitation of the oxalate was varied from 5 to 7 without increasing the error.

Magnesium is determined spectrophotometrically on aliquots of the same ash solutions by the thiazole yellow colorimetric method of Drosdoff and Nearpass. Quantities determined were as low as 10 micrograms. Iron, phosphorus, calcium, manganese and aluminum do not interfere. Wet or dry ashing made no difference in the results.

Results obtained on normal and cancer tissues were presented.

Determination of Invert Sugar. S. G. HINDIN, C. L. OSTERMAN, AND R. W. LIGGETT, American Sugar Refining Co., Philadelphia, Pa.

An adaptation of the Somogyi method for determination of reducing sugars was suggested. The modification entails the spectrophotometric determination of unreduced cupric ion, after removal of cuprous oxide by centrifugation.

The decrease in optical density of the solution after reaction is linear over the range 200 to 600 mg. of invert sugar per liter, within ±1%. Under the same experimental conditions, the reagent is also reduced in the presence of large amounts of sucrose. This effect varies slightly with the invert sugar-sucrose ratio, but for any given ratio it remains constant. In the determination of invert sugar in the presence of sucrose, application of the previously determined correction factor gives data of the same order of accuracy as in the absence of sucrose—i.e., ±1%.

Unlike most reducing sugar methods, results obtained are almost completely insensitive to variations in operator technique.

Rapid Semimicrodetermination of Oil in Refinery Waste Waters. A. F. S. MUSANTE, Sun Oil Co., Marcus Hook, Pa.

Contrary to popular belief, oil and water do mix, and the resulting mixture represents a loss of product as well as a serious

pollution problem in the petroleum industry. Because the evaluation of any pollution-abatement process requires determination of the oil content of many waste water samples, the development of a rapid reliable method was undertaken.

A comparative study of existing oil determination methods showed that extraction with a solvent was the most direct but was subject to large errors due to ineffective extraction in separatory funnels, and loss of oil on evaporation of solvent from evaporating dishes. These shortcomings were corrected by substituting a high speed stirrer in the extraction step and distillation from a flask in the removal of solvent from extract.

The waste water sample is extracted in a gallon bottle with two 150-ml. portions of benezene using a high speed stirrer for agitation. The benzene and water layers are separated after each extraction by transferring to a separatory funnel. The resulting benzene extract is first reduced to about 5 ml. by rapid distillation from a simple still on a hot plate and the residue transferred to a miniature still for the complete removal of solvent; the cut point is determined by thermocouple and potentiometer. The residue is weighed and results are reported as parts per million by weight, assuming 1 ml. of water sample to equal 1 gram.

Results within 5% of theoretical were obtained on samples of known compositions containing oils boiling above 300° F. The time required per determination is about one hour and the method is readily adaptable to multiple simultaneous determinations.

Concentric-Tube Fractionating Columns. C. K. DONNELI AND R. M. KENNEDY, Sun Oil Co., Norwood, Pa.

A concentric-tube fractionating column has been used for several years on a routine basis for the precise fractionation o very small samples of complex mixtures such as alkylates. The column has an annular space 0.75 mm. wide and is approximately 900 mm. long. It develops a minimum H.E.T.P. of 5 to 6 mm. equivalent to about 160 theoretical plates, at a boilup rate of 3C to 60 ml. per hour. The total operating holdup is only 2.5 ml., sc that samples as small as 15 ml. can be effectively separated. Fractions of 0.5-ml. volume are generally collected, then analyzed for their individual components by means of infrared spectra. The still pot, fractionating column, and still head are all enclosed in a single silvered vacuum jacket to reduce the heat loss to a minimum. Samples boiling from 25° to 150° C. can be distilled with no auxiliary jacket heat. With the aid of a Glascol column heater, samples boiling well above 200° C. can be handled.

The results of fractionating efficiency tests using methylcyclohexane–n–heptane and methylcyclohexane–iso-octane mixtures were presented. The relationship of the holdup, pressure drop, and H.E.T.P. to the boilup rate was shown graphically. The results were compared with two theoretical equations derived by Westhaver and Kuhn which relate the H.E.T.P. to vapor velocity, annulus width, and diffusion coefficient of the mixture. Two typical distillation curves were presented to show the results obtained in routine use.

North Jersey Meeting-in-Miniature

THE First Meeting-in-Miniature of the North Jersey Section' AMERICAN CHEMICAL SOCIETY, held in Newark, N. J., on January 10, was divided into organic, industrial and engineering, analytical, and polymer groups. The papers presented before the analytical group are abstracted here.

Colorimetric Determination of β-Pyridyl Carbinol. E. G. WOLLISH, G. P. KUHNIS, AND R. T. PRICE, Hoffman-La Roche, Inc., Nutley, N. J.

Because β-pyridyl carbinol showed a distinct vasodilating action in clinical investigations, a method for its assay in pharmaceutical preparations was desired. A colorimetric method was therefore developed.

The procedure is based upon an adaptation of the Koenig reaction [*J. prakt. Chem.*, 69, 105 (1904)]. With the α-position of the molecule unoccupied, this pyridine derivative can react with cyanogen bromide and an aromatic amine to yield a colored compound. While nicotinic acid will produce a yellow color under conditions of the test [Harris and Raymond, *Biochem. J.*, 33, 2037 (1939)], β-pyridyl carbinol, when heated with cyanogen bromide and p-aminoacetophenone, will yield a purple color upon acidification, which can be utilized for colorimetric measurement.

The specificity of the reaction was discussed. Experimental data were presented, showing the effect of various factors which have a bearing upon the accuracy and precision of the results: concentration of reagents used, temperature, duration of reaction time, pH, and stability of color produced.

Working details were described. Using standards, the optical density is determined at a wave length of 560 millimicrons, and the results are calculated according to Kodicek's formula [Kodicek, *Biochem. J.*, 34, 724 (1940)].

Because the color developed was found to reach a maximum intensity after 20 minutes with subsequent fading, exact timing of all steps is necessary to achieve reproducible results. The method may be applied for the assay of β-pyridyl carbinol in tablets and ampoule solutions.

Stoichiometric Iodometric Method for Determination of Water by Karl Fischer Reagent. WM. SEAMAN, W. H. McCOMAS, JR., AND G. A. ALLEN, Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J.
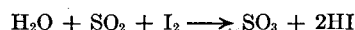
The Karl Fischer reagent for the determination of water, which consists of a solution of iodine in sulfur dioxide, pyridine, and methanol, suffers from two shortcomings: It rapidly undergoes considerable decomposition, thus requiring frequent restandardization, and it must be standardized empirically against water and can not be used on the basis of its iodine content.

A modified Fischer technique was proposed. The reagent is made up and used in the form of two solutions—one containing sulfur dioxide, pyridine, and methanol (for dissolution or dispersion of the sample) and the other containing iodine and methanol (for titration of the water). The water content of a sample is calculated from the iodine contained in the volume of the second solution consumed, according to the equation:

$$H_2O + SO_2 + I_2 \longrightarrow SO_3 + 2HI$$

The iodine solution is standardized with thiosulfate, but its water content must also be taken into account. It is stable if protected from the absorption of atmospheric moisture.

Determination of water in a number of samples by both the usual method and the proposed method indicated satisfactory agreement. Conditions were described under which water may be determined, if necessary, in the presence of excess reagent followed by back-titration with water, with a minimum of decomposition.

Spectrophotometric Determination of Sulfaquinoxaline. CHAS. ROSENBLUM AND JAMES P. DUX, Merck & Co., Inc., Rahway, N. J.

The suitability of the Marshall color reaction as the basis for a spectrophotometric assay of sulfaquinoxaline was investigated using N-(1-naphthyl)-ethylenediamine dihydrochloride as the coupling agent. As Beer's law was not followed rigorously, extinction coefficients were determined at several concentrations. The effects of acidity and salt concentrations on the color intensity were also investigated, and optimum conditions for color formation recommended. The method was applied to sulfaquinoxaline samples of known purity, to certain of its salts, and to mixtures with inorganic diluents.

Bromination of Phenol Resins. H. L. BENDER, A. G. FARNHAM, AND J. W. GUYER, Research and Development Division, Bakelite Corp., Bloomfield, N. J.

Phenolic resins are sold as molding mixtures or varnishes with the resin present in a partly advanced stage. A group of commercial resin converters change these products into hardened form ready for final structural uses. Physical tests of hardening speed, flow, or pressure sensitivity are used to characterize the mixtures ready for conversion. Past chemical tests have been too uncertain for resin definition.

A survey of the bromination technique has resulted in advance in the phenol-aldehyde resins and new lines defined by this technique have been patented and are now in the process of market release.

The reaction of phenol and formaldehyde produces resin chains. The first produced group of such chains has two aromatic rings and gives three crystalline isomers of industrial importance: the 4,4'-, the 2,4'-, and the 2,2'-dihydroxydiphenylmethanes. Bromi-

nation of these gave the clue to technique for using bromination as a resin test. The 4,4' brominated easily, the 2,4' intermediate, and the 2,2' with difficulty.

The subsequent chaining of these crystalline isomers into resins gave, as first members, resinous products of such molecular weights as indicated size equivalent to four aromatic rings. The three crystalline isomers made into such four aromatic ring resins still show differences in bromination rate. Thus the bromination procedure acts to supplement the physical tests of speed and flow for these phenol-aldehyde resins. Analytical details of a proper bromination procedure were disclosed.

A Practical Method for Solubility Analysis. F. A. BACHER, Merck & Co., Inc., Rahway, N. J.

Solubility analysis can give information about absolute purity and can be used as a specific assay method when chemical methods are not available. A practical technique for routine solubility analysis was described. After preliminary trials have indicated a suitable solvent, several sealed ampoules are prepared containing a fixed quantity of solvent and increasing amounts of solid in excess of the amount necessary for formation of a saturated solution. The ampoules are turned end over end in a thermostat for several days and allowed to settle, and the composition of a sample of clear solution from each ampoule is determined by evaporation of the solvent. From data so obtained a plot of solution composition against system composition is constructed for interpretation.

Each analysis, if the system is already known, can be completed in approximately one week, the actual working time being about 3 hours. The method described uses special weighing bottles and a microanalytical balance. It can be adapted to samples as small as 100 mg.; the usual quantity needed is about 1 gram. Hundreds of organic compounds have been tested. Several analyses were described in detail and the results interpreted in terms of purity.

A Thermometric Method for the Determination of Sulfur Trioxide in Chlorosulfonic Acid. WM. SEAMAN, J. T. WOODS, AND H. N. BANK, Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J.

A more precise and specific method was needed for the determination of sulfur trioxide in chlorosulfonic acid than the conventional procedure involving the determination of total acidity and chloride values from which the sulfur trioxide may be calculated indirectly. This need was met by a method which involves measuring the temperature rise that occurs when dry hydrogen chloride, passing through the sample, reacts with the sulfur trioxide and calculating the sulfur trioxide content of the sample from a standard equation.

Over the range 0.4 to 2.8% sulfur trioxide the method has a precision expressed as a standard deviation of ±0.024% (absolute) of sulfur trioxide. There is no reason to believe that there is any systematic error. Sulfuric acid does not interfere, at least in concentrations up to 5%.

For the conditions described 3% sulfur trioxide is the upper limit of the concentration of sulfur trioxide which may be determined by the method, but samples containing as much as 35% sulfur trioxide have been measured by dilution techniques with a precision somewhat better than may be attained by the usual procedure involving the determination of the total acidity and chloride values.

There is some evidence of the existence of the equilibrium:

$$ClSO_3H \rightleftharpoons SO_3 + HCl$$
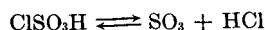
A System of Absolute Quantitative Analysis of Organic Substances by Isotope Dilution and Infrared Spectrophotometry. N. R. TRENNER AND R. W. WALKER, Merck & Co., Inc., Rahway, N. J.

A system of absolute quantitative analysis of organic substances in complicated mixtures such as impure synthetic products or natural crudes by means of isotope dilution and infrared spectrophotometry was described.

Two fundamental principles form the basis of this system of analysis. The first is the application of the well known principle of isotope dilution in which a known amount of an isotopic isomer of the substance for which assay is required is added, as a tracer, to a predetermined amount of the unknown. The sample and tracer mixture is brought to a state of molecular homogeneity by solution in a suitable solvent and then a pure specimen of the isotopically mixed isomers of the substance for which assay is sought is qualitatively isolated. This method of analysis can be utilized

only if a method is known or can be developed for the isolation in pure form of some of the substance of interest. The use of this principle of isotope dilution obviously renders the analysis absolute, as impurities cannot interfere.

To complete the analysis, a measure of the extent of dilution of the isotopic tracer in the isolated specimen is required. This is achieved through the application of the second principle—namely, that the properties of the infrared absorption spectrum of a substance depend, in addition to other factors, upon the masses of the vibrating nucleuses which go to make up its structure. It follows, therefore, that the infrared absorption spectra of any two isotopic isomers will be different, certain of the absorption bands showing marked (greater for isotopes of large mass difference) shifts in frequency in going from the isomer having the lighter isotope to that having the heavier. Such spectral differences enables one, through the use of Beer's law, to determine the tracer dilution spectrophotometrically. Two advantages over conventional methods of isotope assay accrue through the use of infrared spectrophotometry. The purity of the isolated specimen may be inquired into through investigation of its whole spectrum for spurious absorption bands not belonging to either isotopic isomer. Additional manipulative errors are likely to be introduced by conventional methods of isotope assay, such as combustion of the specimen and the like. These are wholly eliminated in this procedure, as the tracer dilution is determined directly on the isolated specimen under conditions such that isotope exchanges, etc., are not possible. With the determination of the dilution of the tracer, the assay is complete and the amount of the substance sought is very simply calculated.

In selecting the isotope for use in this method, several factors must be considered: availability, the extent of the change in the infrared spectrum which its introduction will bring about, and the ease with which it can be synthesized or otherwise introduced into the desired molecule. Fortunately, one isotope, deuterium, adequately fulfills all these requirements. Deuterium is comparatively cheap and available in relatively large quantities. Its mass is twice that of its isotope protium which is present in practically all organic compounds in a relatively large number of atoms. It is, moreover, generally more easily introduced (in nonexchangeable positions) into the average complicated organic molecule than other usable isotopes such as carbon and nitrogen and is, therefore, the isotope of choice for this system of analysis.

By way of illustration of the above principles, the infrared absorption spectra of a number of deutero-organic molecules were presented and discussed. Some methods of "synthesizing" deutero-organics, both chemical and microbiological, were indicated. The application of the above system of analysis to some specific analytical problems was outlined and comments were made concerning the uses of this absolute method for checking the reliability of other secondary and more conventional chemical methods of assay of organic substances. Brief mention was made of the use of certain departures from the above direct method whereby analytically unfavorable spectra (sometimes encountered) may be made favorable by subsequent chemical reactions upon the isolated isotopic isomer mixture.

The Viscosity of Liquid Selenium and the Effect of Additives. H. KOLIN, Federal Telecommunication Laboratories, Nutley, N. J.

Selenium has been reported as behaving erratically in the liquid state. Determination of its viscosity was undertaken in the hope of resolving some of the apparent anomalies reported in the literature. The measurements were made in single capillary Ubbelohde viscometers maintained at temperature in an electrically heated air bath. Unlike sulfur, to which it is related chemically, the viscosity of liquid selenium was found to vary in a perfectly regular manner with temperature. Over the range 224° to 406° C., the viscosity varied from 1950 to 37.5 centipoises. Using the A.S.T.M. equation for the given data, the best linear equation was found to be: $\log \log (V + 0.8) = 0.4783 - 2.976 (\log T - 2.6800)$.

Heat-aging liquid selenium for more than 500 hours at 260° C. did not affect the viscosity. Adding iodine, sulfur monochloride, or mercury in concentrations from 0.5 to 2% lowered the viscosity, the effect generally corresponding to the concentration of additive. The use of mercury as an additive resulted in somewhat erratic viscosity readings.

Determination of Water in Streptomycin by the Karl Fischer Reagent. J. D. NEUSS AND H. A. FREDIANI, Merck & Co., Inc., Rahway, N. J.

The current method for the determination of moisture in streptomycin involves a 3-hour drying under reduced pressure at a

relatively low temperature. This method yields a value which can be duplicated if conditions are very carefully controlled, but which represents only between 20 and 70% of the actual moisture content of the sample. Prolonged drying under similar conditions indicates that the 3-hour period is at a steep portion of the drying curve. If the drying, under these conditions, is maintained for 24, 48, or more hours, the 3-hour value will only roughly approximate the final value. Some samples indicating 1 to 1.5% moisture at the 3-hour period may show as much as 4 or 5% moisture if the drying is sufficiently prolonged. That the total loss is due to moisture plus other volatile solvents is indicated by the fact that samples dried for prolonged periods do have high potency.

The Karl Fischer method has been found to yield reproducible precise results for this determination. A comparison of the values obtained on thoroughly dried samples of streptomycin trihydrochloride, sulfate, phosphate, calcium chloride complex, indicate that the value obtained by the Karl Fischer technique is equivalent to the long-term drying value obtained on the sample. Carried out potentiometrically using the dead-stop end-point technique enables a moisture determination to be carried out on these samples in 5 to 10 minutes. The carbonyl group inherent in the streptomycin moiety apparently does not play a part in the reaction.

Chemical Determination of Folic Acid in Pharmaceutical Products. MARIE JONES AND FRANK O. HOWLAND, JR., E. R. Squibb and Sons, Brooklyn, N. Y.

The Bratton-Marshall reaction, as modified by Hutchings for the determination of folic acid, has been used for the assay of this material in pharmaceutical products through the development of extractive procedures which obtain folic acid free of interfering materials. The relatively small amount of folic acid in these preparations and the presence of interfering materials in high concentration have presented difficulties in the application of this reaction to folic acid combinations; it has, however, been applied to products containing folic acid in the presence of other vitamins, of desiccated liver, and of iron salts in capsules and tablets, as well as those containing only folic acid together with inert ingredients.

Among the procedures being used are (1) extraction of iron salts by means of ether from a 20% hydrochloric acid solution of the sample, a procedure which also removes oils and waxes present in capsule mixtures; (2) increased amounts of reagents in the color reaction to compensate for those consumed by interfering materials; (3) a blank including the sample solution and omitting the colorimetric reagent in the case of highly colored assay solutions; (4) the use of 5-cm. cells instead of 1-cm. cells in determining optical density on the spectrophotometer to permit smaller samples; and (5) the use of ether and a sintered-glass funnel to separate the water-soluble vitamins, including folic acid, from the waxes and oils in capsule mixtures. As no methods for the determination of folic acid in pharmaceutical preparations have appeared in the literature to the present time, detailed procedures were given for the extraction of folic acid from various types of capsules and tablets. Tables showing comparison of assay results and expected values were included.

Colorimetric Determination of Phenobarbital in Tablet Combinations. MARIE JONES AND FRANK O. HOWLAND, JR., E. R. Squibb and Sons, Brooklyn, N. Y.

The reaction of phenobarbital with cobaltous salts in alkaline medium has been used as the basis of simple quantitative methods for the determination of this material in tablets also containing aminophylline, theobromine, or mannitol hexanitrate. Because these compounds interfere with the reaction, the following procedures have been developed to separate the phenobarbital.

Tablets containing aminophylline with phenobarbital are extracted with ether, and, to an aliquot which has been evaporated to dryness, the reaction is applied. Tablets containing mannitol hexanitrate with phenobarbital are extracted with 20% acetic acid, converting the mannitol hexanitrate to mannitol which is insoluble in ether. After neutralizing to a pH of 6.5, phenobarbital is extracted with ether, an aliquot evaporated, and the color reaction applied to the residue. Tablets containing theobromine sodium acetate with phenobarbital have the phenobarbital present as the sodium salt, and are extracted with water. Acidification precipitates the theobromine and converts the sodium phenobarbital to the acid form. It is then extracted with ether, an aliquot evaporated to dryness, and the color reaction applied. The reaction is carried out in the following manner: To the residue in a 10-ml. volumetric flask (representing about 4 mg. of phenobarbital), 1.0 ml. of a 0.5% solution of cobaltous chloride

in methanol is added, the flask is heated on the steam bath 3 to 4 minutes, 2.0 ml. of a 0.5% solution of barium oxide in methanol are added, and the contents of the flask are cooled and made up to volume with methanol. The optical density is determined on a spectrophotometer at 570 mu, the wave length of maximum absorption for the violet blue color formed. Reference to a standardization curve gives the amount of phenobarbital in the sample solution. Over-all accuracy of method is within ±3%.

Spectrophotometric Method for Following Periodate Oxidations

DURING the course of oxidative studies on febrifugine (a natural product of high antimalarial potency) it was deemed profitable to investigate the behavior of certain α-amino alcohols and related compounds when treated with periodate in aqueous solutions at various pH values. Studies indicate that, in the absence of other components absorbing in the near ultraviolet range, the progress of very rapid periodate oxidations may be followed conveniently, even at rather low concentrations, by noting the decrease in optical density of the reaction mixture.

Using dilute (1×10^{-4} M) water solutions of potassium periodate and potassium iodate against water as a blank, it was noted that the former possesses an absorption maximum at 222 mμ, whereas the latter shows no peak in that neighborhood. In the usual periodate oxidations, the reagent is reduced quantitatively to iodate. To ascertain whether or not mixtures containing both periodate and iodate exhibit abnormal absorption, a series of such mixtures was prepared, and their optical densities were determined immediately and plotted against per cent periodate present. It was found that at dilutions of the order 2×10^{-4} M the optical density of an aqueous solution decreases linearly as the per cent concentration of periodate in the mixture is decreased.

Once such a diagram is prepared for any desired initial concentration of periodate and at a known temperature, one can determine the amount of oxidant used up after any period of time by observing the density at that same temperature. Of course, it must be shown beforehand that neither the material to be oxidized nor its oxidation products absorb appreciably at the wave length used. Using this method, rate data on one very rapid reaction, the oxidation of 2×10^{-4} M ethanolamine at 25° C., was obtained. The measurements in this case were made with a Beckman quartz spectrophotometer, equipped with a thermostated cell mounting block. Interpretation of the data will be reported at the conclusion of more complete studies on other compounds.

The method should prove useful for all periodate oxidations with rates too high for the usual type of measurement.

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An Improved T-Tube Pressure Regulator. William N. Carson, Jr.[1], The Ohio State University, Columbus, Ohio.

A T-TUBE whose open end is immersed in a column of liquid is often used for the regulation of pressure. As usually made, the device has several limitations: The liquid is likely to be spattered out with sudden line surges, or is sucked back in the line whenever the pressure falls below atmospheric, and the range of pressure controlled by any one device is limited. The regulator described is simple to build and use, and overcomes these objections.
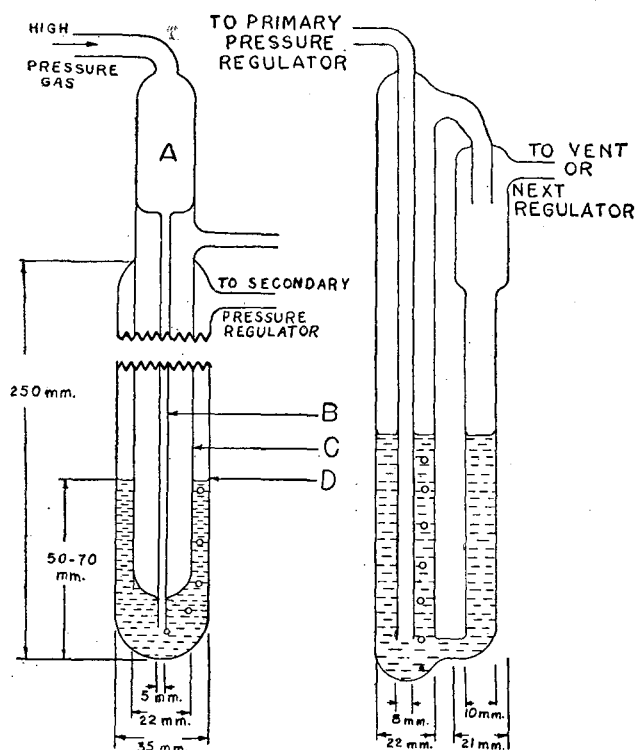
The regulator is divided into two basic components: the primary regulator (left) and the secondary regulator (right).

In the primary regulator high pressure gas enters through trap A, which prevents the liquid in the regulator from entering the line on a suck-back, and continues through the inner tube, B. The emerging gas is collected for the most part in the inner annular space between tubes B and C. This gas is compressed by a combination of hydraulic and pneumatic pressure in the outer annular space between tubes C and D. If sufficient gas is flowing to allow a small excess to be discharged through the outer annular space, the pressure in the inner annular space is held constant to within a small percentage. This pressure is equal to the head of liquid in the outer annular space, plus pressure developed by the secondary regulators. Splashing of the liquid into the discharge line is avoided by use of the long tube of large diameter, which provides a large free space above the surface of the liquid. By using only a small amount of liquid in the regulator, splashing through the vent is avoided.

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Only a small amount of liquid is needed in the primary regulator, as the secondary regulators provide ample pressure in the outer annular space. The range is readily adjusted by the addition or removal of one or more of the secondary regulators. The trap used in the secondary regulators is self-emptying, and readily removes liquids hard to trap from the outgoing stream of gas. The dimensions of the regulators given are those used in the author's laboratory. In the primary regulator, a large free space above the surface of the liquid in both of the annular spaces is necessary, and a large enough trap, A, must be provided. In the secondary regulator, the liquid surge must never cover the tip of the inlet tube, and the tip must be below the outlet tube. The former requirement is met by allowing at least 30-mm. length between the tip and the top of the return tube.

Pressure regulators of this type have been used in the author's laboratory for the past 2 years on systems requiring a constant pressure coupled with large sudden changes in demand for gas. No attention is required after the initial adjustment.

A Useful Stopcock Lubricant. I. E. Puddington, National Research Council, Ottawa, Canada.

A LUBRICANT that will not absorb appreciable quantities of certain organic vapors is frequently required for stopcocks and ground-glass joints in exposed positions. Because it is often inconvenient to regrease these stopcocks, the lubricant should prevent the seizure of the moving parts for long periods of time, and in addition should possess a low vapor pressure.

Anhydrous glycerol which has been thickened with dextrin, bentonite, mannitol, and the like has been suggested frequently for this purpose. The vapor pressures of these preparations are probably satisfactory for most uses, as the vapor pressure of anhydrous glycerol is about 4×10^{-4} at 20° C.; their life in frequently turned stopcocks, however, leaves much to be desired. In an attempt to overcome this difficulty, it was found that finely divided silica incorporated into the glycerol produced remarkable results.

The silica used was in the form of an aerogel (Santocel C, obtained from the Monsanto Chemical Co.). This material was ignited at a temperature of 450° C. overnight to remove traces of volatiles, and then incorporated in small portions into the glycerol until a uniform dispersion containing 20 to 25% by weight was obtained. A Waring Blendor or other stirring device will produce the dispersion conveniently. The glycerol may be rendered anhydrous by heating to about 70° C. for 2 hours in a diffusion pump vacuum. Although this drying procedure may seem somewhat elaborate, it is a worth-while precaution, as it eliminates the annoying and time-consuming dehydration process which occurs at the stopcocks in low pressure systems, when a lubricant prepared from commercial silica and laboratory grade glycerol is used.

After about 20% of silica has been incorporated, the glycerol is an extremely viscous fluid and is sufficiently stringy to resemble a concentrated polymer solution. This dispersion has excellent lubricating properties. In one instance a 6-mm. bore stopcock which had received an application of it was exposed continuously to benzene vapor at 6-cm. pressure for 6 months; at the end of this time, although it had been turned frequently, the stopcock showed no detectable increase in friction and at no time was any streaking visible.