ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

Financing Modern Instrumentation in Academic Institutions

WORD reaches us that the Panel on the Nation's Potential (for research) has been dissolved for lack of funds. The panel was organized under the sponsorship of the Office of Naval Research and its modest expenditures were provided for out of navy funds. The original intent of the panel was to conduct a comprehensive survey of the nation's research assets in the physical sciences and to determine what further was needed to maintain present leadership.

Two preliminary surveys were conducted in an attempt to find out just what facilities and personnel were available in the colleges and universities for fundamental research in chemistry. At this point the decision was reached that it was inappropriate for any government agency to furnish funds for the type of activity the panel came to believe it should undertake. An attempt to raise funds from private sources to permit further study under the sponsorship of the National Research Council failed. The demise of the panel is most unfortunate, for it was expected that the surveys conducted under its auspices would show how funds provided by a National Research Foundation could be used most effectively in support of fundamental chemical research.

At least, the preliminary surveys indicated how poorly equipped colleges and universities are in modern research instruments, confirming, of course, a situation well known to educators. This condition is of special concern to those interested in the future development of analytical chemistry and particularly instrumental analysis.

Private industry can finance the purchase of expensive instruments now essential for fundamental and applied research in analytical chemistry. Indeed, it has found from a strictly financial viewpoint that such expenditures lead to further economies. The colleges and universities, on the other hand, are finding it very difficult to secure adequate funds for the purchase of such equipment.

In the course of a year we visit many university laboratories where our future analysts are being trained. In many instances we find that the equipment available was purchased in the thirties and is not in very good condition. Universities were unable to purchase more modern equipment in adequate quantity during the war years, and now the cost frequently is prohibitive.

The practical effect of this condition is indicated by figures recently disclosed in a private communication from M. R. Fenske of the Pennsylvania State College. In 1931, universities supplied 55%, government agencies 20%, and industry 25% of the papers published in the ANALYTICAL EDITION of INDUSTRIAL AND ENGINEERING CHEMISTRY. However, in 1949, universities provided 40% of the published manuscripts in ANALYTICAL CHEMISTRY, government agencies 20%, and industry 40%.

These figures are not completely conclusive, for the over-all volume of research reported in 1949 is much greater than in 1931, but they do indicate a trend. Advances in applied research in instrumental analysis depend upon continuing advances in fundamental knowledge. It is but natural that we look to the colleges and universities to supply a large share of the exploratory work into physical and chemical phenomena. They will not be in a position to do so if funds are not made available to them for the purchase of necessary instrumentation.

Where is the needed financial support to come from? We believe the colleges and universities would prefer to receive financial aid from private sources, but for reasons that are well known and need not be elaborated upon, the likelihood of obtaining aid from these directions becomes more and more remote under existing tax laws. Even institutions supported by state funds experience difficulties in obtaining money for scientific instruments. Legislatures will provide funds for buildings, but only infrequently are they convinced that sizable sums should be spent on equipment which seems to them to be little more than expensive gadgets.

If financial support cannot be obtained from private sources, the alternative is the Federal Government. Despite recognized dangers, many of our outstanding educators look to the early establishment of a National Science Foundation as the only way out of the present dilemma.

2nd Annual

Review of Analytical Chemistry

CONTINUING our review of developments in analytical chemistry, the following 11 articles report progress in important fields of application. The fundamental developments were reviewed in our January issue. A combined reprint of the reviews from both issues is available at $1.50 per copy from the reprint department of the AMERICAN CHEMICAL SOCIETY.

—The Editors

COATINGS

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IN ACCORDANCE with the plan of last year, this review is concerned with coated organic high polymers and their incorporated oils and pigments. Thinness or discontinuity is not a restriction; so organic finishes for paper, textiles, and leather are included. The reviewers do, however, abbreviate their scope by arbitrarily omitting important protective and decorative coatings such as vitreous enamels, metals, and chemically treated metals. They also temporarily disregard coatings for other uses, such as in welding, optics, lubrication, or friction drives. As before, the term "coating" is construed to imply that the material has been applied and "dried." Coatings which "dry" merely by evaporation of a solvent may be redissolved and analyzed as for the original material, whereas coatings which dry or "cure" by chemical change are generally rendered less soluble and correspondingly more difficult to analyze. Accordingly, analyses of the "insoluble" variety of organic coatings have been the less satisfactory and hence their 1949 improvements are given the more emphasis.

General schemes for the analyses of organic coatings are considered first. Monographs on the analysis of separate parts of such coatings are considered in the order: separate classes of resins, relevant oils, pigments, and specific constituents or functional groups. Auxiliary references to a limited bibliography on relevant descriptive and evaluative literature are presented for the benefit of the analyst who is looking for possible identities of his "unknown" material or general "background" information.

GENERAL ANALYTICAL SCHEMES FOR ORGANIC COATINGS

The reviewers are fortunate to have for a starting point the "paint bible," "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," by Gardner and Sward (*19*). This comprehensive treatment of the subject of coatings, now in its eleventh (1950) edition, is just off the press. It contains 640 double pages of physical tests and chemical analyses. There are 19 chapters, 407 pages, of physical tests mostly for descriptive and evaluative purposes; there are 12 chapters, 218 pages, on the "examination" of coating materials for analytical purposes.

Coating Materials

Chap.		Page
20	Examination of Drying Oils and Oil Seeds	408
21	Examination of Driers and Metallic Soaps	439
22	Examination of Volatile Thinners	446
23	Examination of Resins	463
24	Examination of Shellac	497
25	Examination of Varnishes	509
26	Examination of Bituminous Paints	526
27	Examination of Waxes and Polishes	533
28	Analysis of Paint	537
29	Testing Raw Materials for Cellulosic Coatings	578
30	Physical Tests on Cellulosic Coatings	608
31	Analysis of Cellulosic Coatings	618–625

Tests and procedures appearing after the previous (1946) edition are included at the end of relevant 1946 chapters as addenda. Many of these references (*2, 8, 10, 21, 24–26, 34, 39, 47–49, 52*) are very recent and postdate the predecessor (*41*) of this review. In most instances, the text of these procedures is abridged in Gardner and Sward but will serve as operative directions with the additional advantage of being collected in one book. These references along with others are mentioned again, according to their subjects, in the event that they are desired by and available to the reader.

Other recent books containing pertinent material include the "Modern Plastics Encyclopedia" (*32*), the "Handbook of Plastics," 2nd edition (*43*), "Paint and Varnish Technology" (*17*), and "Analytical Methods for a Textile Laboratory" (*28*).

The analytical format of the 1948 edition of the "Modern Plastics Encyclopedia" (*32*) was covered in some detail in last year's review. The principal innovation for 1949 is the inclusion of an article on the survey of the properties of plastics, which was abridged from a report prepared by the Battelle Memorial Institute for the Office of the Chief of Ordnance and published by special permission. Used in conjunction with the plastics properties chart opposite page 1178, this article, together with some 300 references to domestic and foreign journals which accompany it, is designed to give descriptive information for the synthesist and manufacturer of plastics materials but will also be of determinative value for the analyst of these materials.

The "Handbook of Plastics" (*43*) offers a comprehensive treatment of the plastics field. Chapter XIX on "Analytical Methods" is of particular interest to these reviewers. Prepared by H. E. Riley of the Bakelite Corporation, this excellent discussion is divided into two parts: (1) qualitative identification of resins, fillers, solvents, plasticizers, and other modifying materials; (2) quantitative determination of the composition of the sample.

The first section suggests a general differentiation by the classification of unmodified (or previously isolated) resins according to saponification value and elemental composition. This classification is arranged under nine headings and includes the respective raw materials. There is further differentiation into groups by testing for the elements, and determining acid, saponification, and acetyl values. Eight groups, based on the above tests, are set up in tabular form. The resins falling into each group are still further separated by selective solvents, followed by subsequently detailed tests on the various fractions. After each group there is a tabulation of the behavior of the member resins in response to the specified tests. It appears that the scheme is logical, the tests workable, and the results conclusive. The qualitative portion of the discussion closes with a section on fluorescence analysis, with tabulated results, followed by a series of specific tests for resins and resin constituents, and/or modifiers, including plasticizers and fillers.

The quantitative portion includes directions for a series of general tests, such as the determination of molecular weight, ash, nitrogen, chlorine, phosphorus and sulfur, solids, water, melting point, and viscosity. This is followed by specific determinations for phenolics, ureas, alkyds, polystyrene, polyacrylates, and cellulose ethers and esters. Although physical instrumentation is mentioned in conclusion, the emphasis is placed on materials and apparatus generally available in the average laboratory.

The book (*43*) also includes a comprehensive chapter (XVIII) prepared by Powers and Brother on the "Chemistry of Plastics" which is rich in background information for the resin analyst, and one (II) on the "Properties of Plastics" in which descriptive properties are tabulated and summarized in considerable detail, of potential determinative value.

Because "Paint and Varnish Technology" was not available to these reviewers, the *Materials and Methods* review (*3*) is quoted verbatim:

> This volume presents a survey of the chemistry, formulation, manufacture, and application of paints, varnishes, lacquers, and enamels. It originated as a series of lectures at the Case Institute of Technology, and is of value to those who want an introduction to the entire field, to students of protective coatings, and to manufacturers and users of these coatings. The emphasis is on technological aspects, and many data are given on exposure tests, viscosity, film properties, hiding power, special applications, and surface preparations. Among the chapters are those on: Introduction to the Protective Coatings Industry; Drying Oils; Pigments; Rosin and Rosin Derivatives; Natural Resins and Kindred Products; Testing of Raw Materials; Principles of Paint Formulation; Resin and Varnish Manufacture; Industrial Finishes; Water and Emulsion Paints; Solvent-Type Finishes; Methods of Applying Surface Coatings; and Resin and Varnish Making Equipment.

As for "Analytical Methods for a Textile Laboratory," the review by Harris (*23*) is summarized as follows for the same reason: The handbook is a revision and expansion of materials which last appeared as a supplement to the 1945 A.A.T.C.C. yearbook. New sections on methods of sampling, determination of resins, identification of dyestuffs on fibers, and a bibliography of reference texts on analytical chemistry have been added. Analytical methods selected for this compilation have been chosen for their utility in a textile mill laboratory.

Other books of interest, for which no reviews were available, are included by title in the auxiliary bibliography.

Pertinent papers from the literature are again summarized below under a series of headings.

SPECIFIC CLASSES OF HIGH POLYMERIC MATERIALS

Hanson (*22*) has attacked the analytical characterization of alkyd resins as follows: Alkyds are grouped as oil-free and oil-modified, including natural and synthetic resins as modifiers.

> The discussion under "oil-free alkyd resins" includes a section covering preliminary tests such as dry heating, the phenolphthalein test for phthalic (suitably qualified), fusion with potassium hydroxide, and the Liebermann-Storch test. This is followed by a section on the determination of dibasic acids, usually as the *p*-nitrobenzyl ester prepared from the dipotassium salt, which results from the Kappelmeier saponification of the original resin. This section contains a tabulation of the characteristics of ten dibasic acids, and includes solubility, some color tests, and the melting points of the *p*-nitrobenzyl esters. The final section deals with the determination of polyhydric alcohols, which, after isolation from the saponification mixture, are identified by oxidation with periodic acid, and confirmed by conversion to suitable derivatives. A tabulation of the latter is included.
>
> The discussion of "oil-modified alkyd resins" repeats in part the preliminary treatment, and gives details for the separation of the fatty acid, resin acid, oxidized, and unsaponifiable fractions. Tests applicable to the various fractions are then considered in some detail. A tabulation of results obtainable on oxidized acidic fractions is included, as are some remarks on the applicability of infrared absorption analysis to the differentiation of vegetable oils. The discussion concludes with an outlined scheme for identification.

The whole treatment is authoritative and well arranged. It is necessarily somewhat sketchy, and except for the mention of infrared absorption analysis, relies entirely on chemical procedures, ignoring, rather than excusing, several physical contributions which have been reported and have proved successful in the analysis of such resins.

Clasper and Haslam (*11*), in considering the analysis of nylon and related polymers, start their discussion with a summarized survey of methods which have been reported.

> The hydrolysis of 6,6 nylon is then shown to proceed most satisfactorily by refluxing with 20% hydrochloric acid. The liberated acid is extracted with ether in a specially designed liquid-liquid extractor, and the unwashed ether layer is evaporated to dryness. The amine is recovered as the hydrochloride by evaporation of the aqueous layer. Nylons of the 6,10 variety require preliminary treatment, consisting of dissolution in *m*-cresol, and reprecipitation in a finely divided state by nonsolvent precipitation with methanol. The method was then tried on eight authentic nylon types, using a 40-hour reflux. The results, together with a considerable amount of additional data, are tabulated. The table is supplemented by individual discussions of each of the eight resins, which included a 6,6 polymer, a 6,10 polymer, an unknown 6,6 + 6,10 copolymer, and a 6,6 nylon which had been modified by treatment with formaldehyde and methanol.
>
> A successful method for the separation and estimation of adipic and sebacic acids occurring in 6,6 + 6,10 copolymers consists of a partition procedure, in which the mixed acids are equilibrated with known volumes of water and ether at a definite temperature, and an aliquot of the aqueous layer is titrated with standard alkali. A calculation graph is included. The discussion concludes with several examples of the application of the methods to the analysis of unknown commercial samples.

The treatment is comprehensive and the methods have been worked out thoroughly. Inclusion of details of unsuccessful trials is a refreshing feature. The various attempts are sound, but apparently the help offered by physical instruments has been largely overlooked.

Widmer this year published a group of articles applying and extending the methods of Stafford and co-workers (*45*, *46*) to melamine- and urea-formaldehyde resins in wet-strength paper (*53*) and other technical products (*52*) including laminations and surface coatings. In the first case, Widmer limits himself to commercial papers without surface coatings or impregnation other than the "normal" paper sizes. He abstains from color reactions for the above resins because rosin would interfere. The procedure is:

> (1) Wet-strength test. (*a*) Rubs off, not wet-strength paper. (*b*) Unchanged, wet-strength paper.
>
> (2) Water test. (*a*) Forms drops, rosin probable. (*b*) No drop formation, no rosin.
>
> (3) Storch-Morawsky reaction. (*a*) Positive, rosin. (*b*) Negative, no rosin.
>
> (4) Carbazole formaldehyde test. (*a*) Positive, urea or melamine resin probable. (*b*) Negative, no urea or melamine resin: proteinaceous substance possible.
>
> (5) Nitrogen tests. (*a*) Positive, urea resin, melamine resin, proteinaceous substance possible. (*b*) Negative, No urea or melamine, no proteinaceous substance present.
>
> (6) Differentiation between urea and melamine resin. (*a*) Xanthydrol method: positive, urea resin. (*b*) Sublimation method: sublimate, melamine crystals; melamine picrate—positive, melamine resin.

In the second investigation (*52*), melamine and urea resins on textiles are identified by the same procedure and likewise for filings or scrapings from the "glue line" of laminates.

Alkylated melamine and melamine ester resins oftentimes are not sufficiently hydrolyzed in the usual boiling in 80% acetic acid for 30 minutes. Therefore, the surface coating is pretreated with boiling alcoholic 5% sodium hydroxide for a few minutes. After adding water and boiling off the alcohol, the melamine resin is hydrolyzed by boiling in concentrated hydrochloric acid for 2 minutes and tested as usual.

All the procedures appear logical and workable, but it is the reviewers' opinion, judging from the many photomicrographs, that dendritic crystals, identified merely by measuring the terminal angles, might be risky. If better developed crystals cannot be obtained by stirring the peripheral, dendritic encrustation back into the drop of solution, a couple of recrystallizations from decanted solution drops might be insisted upon.

Several other papers have been published on the detection of groups of resins (usually amine aldehyde condensation products) on fibers. Aenishaenslin (*1*) suggests a procedure for identifying formaldehyde-resin finishes on cellulose fibers and wool; Bernegger (*6*) gives directions for the detection of thermosetting resins on viscose fibers; and Ernst and Sorkin (*15*) present a detailed scheme for the qualitative and quantitative determination of the amount of resins on fibers. The details of these procedures are given in *Chemical Abstracts*.

Wright (*55*) reports on a series of color tests applicable to shellac and other natural resins. Gordijenko and Schenck (*20*) extend their original investigation (*41*) of the detection of complex organic compounds. Wiley and Hobson (*54*) present a critical review of the literature on the determination of the refractive index of polymers, and describe the use of cadmium borotungstate as contact liquid.

A recent advance in resinography, the graphic or pictorial study of resins and their plastics, is the technique of fracturing an embrittled resin, replicating the fracture surface and micrographing the replica at a commensurate resolving power with an adequate microscope (*40*). Although the fracture, accidental or experimental, may be of interest even with a light microscope, most interest, by far, is in the electron microscopical structure. Fundamental units only hundreds of Ångströms in diameter are revealed and these are well within macromolecular dimensions. Because fracture between, rather than across, molecules is inferred in the definition of molecules, one can readily conclude that these fundamental units are the macromolecules themselves. Even with limited practical resolution and scant empirical data, characteristic differences, at least among very chemically different resins, have been observed and it is natural to hope for great determinative and descriptive value from the method, including macromolecular weight distributions, variations in shape with chemical and physical variations, unipolymers among copolymers, and other heterogeneities. Perhaps even more promising to the practical coatings technologist is the revelation of other phases within the resin such as pigments, fillers, reinforcing agents, etc., and in their practical environment, in commercial formulations. The method is already being used to show the distribution of the pigment particles in cured paint films.

There also appeared this year a series of reviews, including contributions by Wheeler (*51*), Fuller (*18*), Van Loo (*50*), and Barnett (*4*), on progress in the protective coatings and plastic industries, which are well worth the attention of the analyst of coatings.

OILS

The subject of oils is well covered in the annual review by Piskur (*36*, *37*). The papers of analytical interest are concentrated in Part II of his current review. Of additional interest is the publication by *Industrial and Engineering Chemistry* of a symposium on drying oils which included Passino (*35*), Bolley (*7*), Cowan (*12*), Powers (*38*), Bradley and Tess (*9*), and Elm (*14*) as contributors.

PIGMENTS AND DYES

In a discussion of the application of physical methods to the analysis of inorganic pigments, Schmidt (*42*) demonstrates that the use of potentiometric, polarographic, and spectrographic methods simplifies and improves the analysis of inorganic pigments, and gives several examples. Munk (*33*) discusses the optical properties of white pigments and coatings and their evaluation. In a detailed treatment of the qualitative analysis of dyes, Mathewson (*31*) presents an authoritative discussion which includes sections devoted to solvents, separation of dyes by fractionation, qualitative examination, identification of separated dyes, bromine oxidation test, reactions of dyes with divanadyl trisulfate in concentrated sulfuric acid, and color changes of dyes with solutions of sodium hydrosulfite. The paper includes tables on relative solubilities of dyes in immiscible solvents, dyes with their chemical names listed in the order of their numbers as given in the "Colour Index," color changes of solutions of dyes with hydrochloric acid and with sodium hydroxide, color changes of dyes with sodium hydrosulfite, colors of solutions of dyes in concentrated sulfuric acid, and color changes of the sulfuric acid solutions on addition of divanadyl trisulfate, and a table comprising the latter two headings as related to vat dyes.

SPECIFIC CONSTITUENTS

This section includes separate constituents of coating materials. Kröller (*27*) uses the characteristic precipitate with mercuric acetate to identify adipic acid. Bennett (*5*) reports on three recommended methods for the detection of formaldehyde. Dietmann (*13*) presents a review of qualitative tests for differentiation of glycerol and glycol.

Swann (*48*) suggests a new procedure for the determination of dibasic acids in alkyd resins, using as starting materials the insoluble potassium salts obtained by a modification of the Kappelmeier procedure. The various acids considered are isolated quantitatively by selective precipitation of the appropriate heavy metal salt. A new technique for accurately determining the nonvolatile content of resins, needed for calculating the dibasic acid content, is included. The Swann procedure is currently being tested cooperatively by Subcommittee XI, Committee D-1, of A.S.T.M. Stafford, Francel, and Shay (*44*) propose a method for the identification of dicarboxylic acids in polymeric esters. By refluxing polymeric esters with benzylamine in the presence of a catalyst, characteristic derivatives of the constituent dicarboxylic acids can be obtained. The resulting dibenzylamides can be separated into saturated and unsaturated fractions by the use of selective solvents. Individual dibenzyl amides can be identified in admixture by comparison of their infrared spectra with those of a standard set of dibenzyl amides prepared from monomeric esters.

The paper chromatographic techniques of Fink and Fink (*16*) and of Lugg and Overell (*29*), as applied to the qualitative analysis of organic acids, represent a potential method of analysis for acidic coating constituents. The details of the procedures are given in *Chemical Abstracts*. The very recent work of Marvel and Richards (*30*), on the separation of polybasic acids by fractional extraction, is another potential method for the acidic constituents of coatings.

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ESSENTIAL OILS AND RELATED PRODUCTS

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THIS second review of analytical procedures for essential oils and related products follows the general outline established in the first of the series (*39*). Discussion is again restricted to several important publications of interest to the essential oil chemist, and to a report on analytical procedures that have been suggested or evaluated during the year. However, reference is made to several earlier papers which have been reported only recently in *Chemical Abstracts;* publications which were not included in the first review are discussed here.

In general, no basically new analytical procedures have been reported for essential oils and related products. Spectral absorption techniques have long been in use in research laboratories for identification of essential oil constituents and for elucidation of structure. Recently such methods have been applied commercially to the analytical control and evaluation of several products in this industry, notably β-ionone. Further developments along this line may be expected in the future.

OFFICIAL COMPENDIA

The publication of the fourteenth revision of the Pharmacopoeia of the United States and the ninth edition of the National Formulary was expected during the year; but it now appears that these two important compendia will not be issued until 1950.

The British Pharmaceutical Codex 1949 (*13*) replaced the 1934 edition, following closely the publication of the British Pharmacopoeia 1948 (*14*). This latest revision of the Codex includes supplementary informative data for the following items which are official in the British Pharmacopoeia 1948:

	Page
Essential oils	
Purified volatile oil of bitter almonds (free from prussic acid)	565
Oil of anise	567
Oil of cajuput	573
Oil of caraway	575
Oil of chenopodium	579
Oil of cinnamon	580
Oil of clove	575
Oil of coriander	582
Oil of dill	566
Oil of eucalyptus	585
Oil of lavender	593
Oil of lemon	595
Oil of nutmeg	602
Oil of peppermint	598
Oil of rosemary	611
Oil of turpentine	618
Synthetics and isolates	
Benzyl alcohol	62
Benzyl benzoate	146
Camphor	197
Ethyl oleate	55
Eucalyptol	332
Menthol (*l*- or *dl*-)	517
Methyl salicylate	529
Terpineol	895
Thymol	914
Balsams, etc.	
Balsam of Peru	128
Balsam of Tolu	129
Benzoin	144
Oil of cade	572
Myrrh	544
Purified storax	860

In addition, monographs (with specifications and standards) are presented for 28 essential oils and for 11 other items of interest to the essential oil trade:

	Page
Essential oils	
Oil of bay	601
Oil of bergamot	570
Oil of sweet birch	571
Oil of camphor, rectified	573
Oil of cardamom	574
Oil of cassia	576
Oil of cedarwood	577
Oil of chamomile	568
Oil of citronella	581

	Page
Oil of cubeb	584
Oil of fennel	586
Oil of Siberian fir	564
Oil of geranium	586
Oil of juniper	592
Oil of lemongrass	588
Oil of *Melaleuca* (tea tree)	597
Oil of mustard, volatile	616
Oil of neroli	603
Oil of orange	569
Oil of pimento	605
Oil of pine, steam distilled	606
Oil of *Pinus pumilio*	606
Oil of rose	610
Oil of sandalwood	612
Oil of sandalwood, Australian	613
Oil of sassafras	614
Oil of spike lavender	594
Oil of thyme (origanum)	621
Synthetics and isolates	
Dibutyl phthalate	295
Diethyl phthalate	56
Dimethyl phthalate	312
Eugenol	334
Safrole	778
Saponin	787
Terpin hydrate	896
Vanillin	941
Balsams, etc.	
Oil of amber	617
Oil of birch tar	612
Copaiba	270

NEW TEXTS AND PUBLICATIONS

During the year several works have been published which are of importance to the essential oil chemist.

The second volume of Guenther's "The Essential Oils" (*38*) appeared in March. This volume, written by Guenther and Althausen, contains descriptions of practically all known constituents of essential oils. Each compound is discussed under the headings of occurrence, isolation, identification, properties, and uses. A supplementary section, by Sterrett, describes the preparation of derivatives of essential oil constituents. This volume should prove of great value not only to the research worker but also to the analytical chemist.

The third volume of this work (*37*), which appeared in November, consists of a series of monographs on the individual essential oils of the families *Rutaceae* and *Labiatae*. Many analytical data are included; the author draws not only upon the literature but also upon his personal experience and upon the extensive analytical records of Fritzsche Brothers, Inc., for establishing reliable analytical limits for these essential oils. This volume represents a long-awaited and up-to-date treatise on the commercially important essential oils of these two botanical families.

The "Givaudan Index" (*33*) is best described by its subtitle: "Specifications of Synthetics and Isolates for Perfumery." It is a much-needed compilation of analytical data for some 254 commercial products of perfumery grade. Each item is arranged alphabetically by its commercial name. Specifications are given for specific gravity, refractive index, purity (and method of determination), solubility in dilute alcohol, and other tests that are applicable to the individual product; other pertinent data are included. A short chapter is devoted to certain recommended analytical procedures to which the reader is referred in the individual monographs. The data are arranged in outline form.

Another "Annual Report" (*77*), covering the year 1946, has been issued by Schimmel & Co. of New York.

The *Berichte von Schimmel & Co.* (*78–82*) covering the war years have become available through an adequate review in the *Perfumery and Essential Oil Record* (*1, 3*). The 1939, 1940, 1941, and combined 1942–43 editions have been reviewed, but as yet no review has appeared for the combined 1944–47 editions.

The Scientific Committee of the Essential Oil Association of the United States has drawn up new standards and specifications (*28*) for two essential oils and six aromatic chemicals. "Determination E. O. A. No. 1-H" has also been proposed; it describes in detail the procedure to be followed for the determination of congealing point. The specifications and the determination have been approved by the membership of the association and will be published in loose-leaf form, ready for distribution early in 1950. This is a continuation of the program initiated in 1946. The new "Specifications and Standards" include the following:

- Essential oils
  - Oil of lavandin
  - Oil of sage Dalmatian
- Synthetics
  - Acetophenone
  - Anisic aldehyde
  - Diphenyl oxide
  - Ethyl phenyl acetate
  - Methyl acetophenone
  - Methyl phenyl acetate

Publication of the well-known periodical *Deutsche Parfümerie-Zeitung* has been resumed under the new title of *Parfümerie und Kosmetik* (*69*).

ANALYTICAL PROCEDURES FROM SCIENTIFIC AND TECHNICAL LITERATURE

Acids. Ramsey and Patterson (*73*) extended their earlier work on the separation of saturated straight-chain fatty acids by partition chromatography to include the C_{11} to C_{19} acids. Green (*35*) studied the estimation of several official salts of weak organic acids in nonaqueous media; as solvent, he used a propylene glycol–isopropyl alcohol mixture (1 to 1) and found the results to be satisfactory for acetates, benzoates, and salicylates, when titrated with a standard solution of perchloric acid in the propylene glycol–isopropyl alcohol mixture. Hubacher (*47*) reported an analytical procedure for the determination of carboxyl groups attached to an aromatic nucleus; his method is based on the fact that such groups can be split off quantitatively as carbon dioxide by heating the acid in quinoline solution in the presence of basic cupric carbonate or other catalysts.

Alcohols and Phenols. Terent'ev and Shor (*86*) suggested several minor modifications for the determination of active hydrogen by means of a Grignard reagent in an atmosphere of carbon dioxide; these modifications were reported to give more accurate results than those obtained with the earlier techniques employed by Terent'ev and his collaborators. Hochstein (*43*) has made a careful study of the possible replacement of the Grignard reagent by lithium aluminum hydride for the determination of active hydrogen; satisfactory results were obtained with glycols, phenols, and amines. Data were presented with reference to the types of compounds which undergo reduction as well as replacement of active hydrogen. The use of lithium aluminum hydride should make the determination of active hydrogen considerably more attractive to the analyst and therefore more widely employed. Zaugg and Horrom (*93*) have confirmed the advantages of the use of lithium aluminum hydride for determining active hydrogen in a comparison with methyl magnesium iodide; they found the hydride to be superior in most of the thirteen compounds examined.

Johnson (*49*) proposed a variation of the acetyl chloride procedure for the determination of hydroxyl groups in organic compounds; however, for many sensitive alcohols it would appear that the acetic anhydride method is preferable. White and Dryden (*91*) studied the separation of forty pairs of aliphatic alcohols C_1 to C_6 by chromatic adsorption of their 3,5-dinitrobenzoates; the technique of Brockmann and Volpers was used. Kochi (*51*) suggested a rapid quantitative method for the determination of terpene alcohols in essential oils based on solubility of oxygenated constituents in 40% sodium salicylate solution; the method is not specific for the hydroxyl group and hence will prove of only limited value.

For the determination of linaloöl, Gottlieb (*34*) proposed the use of dry oxalic acid as a dehydration catalyst; the volume of water formed is measured and the linaloöl content is calculated from this value; there is no indication that oxalic acid is superior to many other catalysts that have been suggested previously by other workers. Kobayashi (*50*) reported on a method for the determination of menthol in mint oils (*Mentha arvensis*) widely used in Japan. This method is based on a comparison of the behaviors of the sample and of several standard oils when subjected to cooling. The menthol contents of the standard oils are determined in the usual manner from the ester number and ester number after acetylation. It would appear that a method based on the congealing point would be very advantageous for *Mentha arvensis* oils and possibly also for peppermint oils (*Mentha piperita*), because it would be an indication of the true menthol content. Further investigation of this possibility should be undertaken. Hoffmann and Maffei (*45*) made a comparison of three standard methods for the determination of linaloöl—i.e., the Fiore method, the Glichitch method, and the Boulez method. They reported that the last method gave low results but that the first two methods gave analytical results within 5% of each other. This investigation again points out the importance of specifying the method of analysis used in an assay for constituents of essential oils.

In a study of the determination of thymol and carvacrol in Spanish thyme oils, Langenau (*52*) described the behavior of known mixtures of thymol and carvacrol when supercooled and seeded, as well as the behavior of such mixtures after separation and regeneration from reconstituted thyme oils; the procedure in general followed that of Sage and Dalton but the results obtained differed greatly from those of the earlier work. It was suggested that this discrepancy may be due to the possibility that the carvacrol of Sage and Dalton contained substantial quantities of thymol. Barcelo (*5*) reported on Spanish thyme oils; he described qualitative tests using ferric chloride to indicate the presence of thymol and carvacrol in the oil. For the quantitative determination, an iodometric procedure was recommended; this method, however, does not appear to be entirely satisfactory for routine analysis. Caujolle and Couturier (*17*) proposed the use of a saturated aqueous solution of sodium thymotate for the separation of oxygenated constituents of essential oils, if only small amounts of terpenes are present; the whole oil is dissolved in the solution and the terpenes are separated by the gradual addition of water. Other applications were suggested; thus the phenolic portion of thyme oil can be separated into a thymol fraction and a carvacrol fraction by this method.

Aldehydes and Ketones. White (*90*) suggested a chromatographic technique for the separation of aliphatic carbonyl compounds; he recommended the use of Volclay bentonite (325-mesh) for the separation of the 2,4-dinitrophenylhydrazones. Results were reported on a study of twenty-two pairs of derivatives involving twelve aldehydes and ketones. Wearn, Murray, Ramsey, and Chandler (*89*) suggested the use of *m*-phenylenediamine dihydrochloride for the colorimetric determination of certain α,β-unsaturated aldehydes. This reagent was reported to be specific for α,β-unsaturated aldehydes and ketones, although a few other highly reactive aldehydes interfere. Procedures are given for the determination of cinnamic aldehyde, croton aldehyde, and furfural without interference from acetaldehyde or benzaldehyde. Hoffmann (*44*) has compared the Stillman-Reed method employing free hydroxylamine at elevated temperatures with the standard hydroxylamine hydrochloride method at room temperature; he confirmed the well-known fact that the former method gives much higher results for the determination of aldehydes in orange oils. In another study (*46*) of these two methods in the determination of menthone in mint oil, the hydroxylamine hydrochloride method at room temperature gave values from 1.7 to 6% lower than the Stillman-Reed method; Hoffmann recommended the use of the latter for this determination.

Petit (*70*) reported on a new method for the estimation of aldehydes and ketones using *p*-nitrophenylhydrazine; the insoluble derivative is treated with a known amount of stannous chloride or potassium stannate solution, in excess, to reduce the nitro group, and the excess stannous ion is determined with iodine. The method appears somewhat cumbersome and inadequate for general use with mixtures as complex as essential oils. For the estimation of aldehydes and ketones, Rao (*74*) proposed the use of hydroxylamine hydrochloride in 60% ethyl alcohol and the subsequent titration of the liberated hydrochloric acid with a standardized potassium hydroxide solution in 60% ethyl alcohol. This modification is neither novel nor generally applicable, for many of the essential oils evaluated by the standard hydroxylamine hydrochloride method are not soluble in such dilute alcohol.

In a review dealing with vanillin, Rutten (*76*) described, among other things, the analysis of this aldehyde. Englis and Manchester (*26*) pointed out a possible source of error in the determination of vanillin by colorimetric or ultraviolet absorption methods; they reported that in the dilute solutions employed, vanillin is readily oxidized to vanillic acid by atmospheric oxygen. This source of error should also be considered when dealing with other easily oxidizable aldehydes. Halpern (*41*) pointed out that the use of a potentiometric end point greatly facilitates the determination of aldehydes when hydroxylamine or neutral sulfite methods are employed; the use of potentiometric titration is especially valuable when using the Stillman-Reed technique.

For the separation of aldehydes and ketones from tars, Pronina (*72*) recommended a technique involving adsorption of the semicarbazones from a petroleum ether solution of the tar by means of silica gel; after the column is washed with petroleum ether until the effluent is colorless, the adsorbed semicarbazones are then eluted with ether. This method, with modifications, would appear to be applicable to essential oils. Naves and Bachmann (*64*) reported on the rates of reaction for the oximation of the cis and trans isomers of α-irones. In a further study of the irones, Naves (*61*) reviewed the techniques of ozonolysis; a micromethod is described correcting in part the errors of the Doeuvre procedure; results between 92 and 102% of theory can be obtained with the modified technique. Greene (*36*) described the behavior of catnip oil when treated with phenylhydrazine reagent, observations being made under a microscope using ordinary and polarized light. Fuchs and Matzke (*32*) reported on the determination of aromatic aldehydes by means of hydrazine sulfate; this reagent is now readily available in commercial quantities, so that procedures employing it may gain in popularity. Rees and Anderson (*75*) described a method for the determination of benzaldehyde in the presence of benzyl alcohol by the use of ultraviolet absorption measurements at 283 mμ.

For the determination of the bromine number of aldehydes, ketones, and acids having unsaturation in the α-position, Petrova (*71*) recommended a modification of the Kaufmann and Barick method; instead of titrating the excess bromine with sodium thiosulfate, he preferred the use of an alcoholic solution of anethole. This modified method proved satisfactory for following the rates of reaction of formation of cinnamic aldehyde and of isomerization of pseudoionone to α-ionone. The use of a mercaptan for the determination of α,β-unsaturated carbonyl compounds (and certain others) has been reported by Beesing, Tyler, Kurtz, and Harrison (*6*); the excess of dodecanethiol was established by titration with standardized iodine solution. Satisfactory results were reported for maleates, crotonates, and aldehydes, but ketones gave only approximate values. Wurtzschmitt (*92*) reported that maleic acid and its esters liberate sodium hydroxide when treated with aqueous sodium sulfite; this represents a possible interfering substance for the determination of aldehydes and ketones by the neutral sulfite method.

Terpenes. In a report on the difference in behavior of β-ocimene and its isomer, myrcene, Crabalona (*19*) pointed out that β-ocimene takes up 6 atoms of bromine compared to 4 for myrcene during the determination of the bromine number. An attempt to correlate the Diels-Alder values using maleic anhydride and *p*-benzoquinone as reagents proved unsuccessful for essential oils, *inter alia*, according to Carrera (*16*).

Isothiocyanates. A rapid determination of organic isothiocyanates (and isocyanates) was proposed by Siggia and Hanna (*84*). This method is based on reaction with butylamine in dioxane and the subsequent titration of the excess amine with sulfuric acid. For the determination of allyl isothiocyanate, Cavicchi (*18*) suggested a new method based on oxidation with bromine. For determining isothiocyanates in the presence of isomeric thiocyanates, Böhme (*8*) proposed a method based on oxidation with hydrogen peroxide and final precipitation of the sulfuric acid formed as the barium salt. All the above methods may have special applications, but probably none will replace the official determination of the National Formulary. For the estimation of mustard oil in dry mustard seeds and other plant material, de la Vega and Capillas (*88*) pointed out the possibility that the natural enzyme, myrosine, may have been inactivated, giving rise to apparently low results.

Peroxides. In a continuation of the study of the assays of ascaridole in wormseed oil, Halpern (*42*) investigated the iodometric method. A rapid release of iodine during the first minute, followed by a further slow, steady release, was observed. Halpern concluded from his study that the nonstoichiometric behavior of ascaridole toward potassium iodide in the determination cannot be explained satisfactorily by the simple iodination of the olefins. This work again points out the importance of following rigidly all conditions of an analytical method when applied to essential oils. Lepetit (*53*) also investigated the methods of ascaridole determination and recommended the technique of the French Codex, which differs but slightly from the official method of the United States Pharmacopoeia. He reported that the empirical factor (0.0084) used in the Codex is much too high, and that the factor of the United States Pharmacopoeia and the British Pharmacopoeia (0.0065) is also high. This author recommends the use of the factor 0.00605 for determinations of ascaridole in normal wormseed oils. Most investigators who have worked with this method are in agreement that the official factor is incorrect; Lepetit is the first to suggest a specific figure.

In two papers, Breit (*11, 12*) reported on the standardization of titanium trichloride solutions; three methods were evaluated with the aid of nine collaborators. Consistent results were obtained with potassium dichromate in the presence of diphenylamine indicator; such standardization proved to be more satisfactory than potassium permanganate as specified by the Association of Official Agricultural Chemists (*4*). Titanium trichloride solution is used in one of the standard determinations of ascaridole.

Determination of Essential Oil Content. McKern and Smith-White (*55*) described a new trap of the Clevenger type for the determination of essential oil content of botanicals; the calibrated collecting tube is removed from the main stream of circulating water to prevent carry-back of large globules of oil to the still. This carry-back is occasionally very troublesome when the Clevenger trap is used, especially if the oil being distilled has a specific gravity close to that of water. For the isolation of plant constituents, Curts and Harris (*21*) proposed the use of ethylene glycolmonoethyl ether (Cellosolve); their experiments indicated that this solvent will extract all those plant constituents normally extracted by petroleum ether, diethyl ether, chloroform, and alcohol. Subsequent stepwise additions of water to the extract will separate various constituents. The use of a single solvent should prove very convenient to experimenters working with botanicals and other natural products.

Determination of Water. Deahl, Powers, and Green (*22*) have studied the drying conditions of the United States Pharmacopoeia, thirteenth revision, and the National Formulary, eighth edition; they found that drying at elevated temperature (105° C.) and normal pressure gave satisfactory results for most products and was generally preferable to drying over desiccants such as sulfuric acid. In drying botanicals, oleoresins, etc., the use of a desiccant is frequently advisable, because heating often causes loss of essential oil. Johnson (*48*) discussed methods empoyed in an industrial laboratory for the estimation of water; the Brabender moisture tester, the effect on freezing point of phenol, the Dean-Starke distillation method, and the Karl Fischer technique all gave satisfactory results. The last two methods are frequently used in the essential oil industry. Fischer (*30*) described three tests for the microqualitative determination of water; these tests must be interpreted with care if applied to essential oils, because the reagents employed are apt to cause dehydration of sensitive constituents, notably tertiary terpene alcohols. Seaman, McComas, and Allen (*83*) discussed the determination of water by the Karl Fischer reagent; they proposed the use of two solutions, one containing pyridine, sulfur dioxide, and methanol to dissolve or suspend the sample, the other containing iodine and methanol for titration. These solutions are stable, so that the necessity for frequent restandardization of the Karl Fischer reagent become unnecessary. Mitchell and Smith covered the use of the Karl Fischer reagent in a text (*58*).

Detection of Adulterants. Naves (*60*) pointed out that in the estimation of the ethyl alcohol content of rose oil from the Zeisel number, a source of error is the presence of eugenol and methyl ether of eugenol; these normally occur to the extent of 1 to 1.2% as natural constituents. Opfer-Schaum (*67*) described a microtechnique for the detection of glycerol; this method is based on the oxidation to acrolein and the subsequent formation of the *p*-nitrophenylhydrazone. In a comprehensive review, Meyer, Massatsch, and Kuntze (*57*) described methods of detecting glycerol, ethylene glycol, diethylene glycol, and propylene glycol. Boos (*9*) improved the chromatographic acid procedure for the microdetermination of methyl alcohol by proposing the measurement of transmission at 580 mμ. Bertrand and Silberstein (*7*) investigated the test for methyl alcohol in the presence of ethyl alcohol, which is based on an oxidation with potassium permanganate and subsequent testing by the Schiff reagent; for routine analytical control, this technique is not as satisfactory as the well-known chromatographic acid procedure. Newburger (*65*) described in detail a method for the determination of castor oil in lipsticks; this appears to be readily adaptable to essential oils and related products. Naves (*63*) discussed methods of distinguishing between pure and adulterated petitgrain oils and also neroli bigarade oils.

Miscellaneous. The laboratory of Fritzsche Brothers, Inc. (*31*), reported a rapid method for the estimation of anethole in anise and fennel oils; mixtures of known anethole-limonene content were prepared containing 55 and 100% anethole and the congealing points determined. When plotted, the resulting curve proved to be essentially a straight line. This method is satisfactory for an approximate estimation.

For the detection of heavy metals, several new procedures were proposed. The use of benzohydroxamic acid has been recommended; for details, the reader is referred to the papers of Musanté (*59*) and Trujillo (*87*). Häberli (*40*) described a colorimetric determination of arsenic in pharmaceutical preparations.

Englis and Reinschreiber (*27*) evaluated by potentiometric titration the official procedure for the determination of saponification number; the investigation confirmed the correctness of the conditions prescribed by the Association of Official Agricultural Chemists.

Maurel (*56*) described a new method for the determination of methyl anthranilate in essential oils; the amine is diazotized and coupled with R acid to produce an intense color which is compared with known standards. For the determination of indole, the same author (*56*) recommended a colorimetric procedure using *p*-dimethylaminobenzaldehyde. These tests must be applied with discretion.

Bradbury (*10*) suggested a modification of Elek and Harte's method for the microdetermination of acetyl groups.

Dobran, Acker, and Frediani (*25*) reported refractive index measurements for many official solids, gums, resins, and waxes at temperatures above their melting points.

Taylor (*85*) presented a table of corrections to be applied to essential oils and related compounds in order to convert the specific gravity to "weight per ml. at 20° C." as required by the British Pharmacopoeia 1948; these corrections are based on a general average for the change in specific gravity (0.00064 per degree centigrade). This will introduce a slight error if the value for the individual oil varies appreciably from this average figure. Lipkin, Mills, Martin, and Harvey (*54*) described the design of two types of pycnometers for determining the specific gravity of oils; the advantages of the cup type and the side-arm type were discussed.

Flash points for essential oils and for certain synthetics and isolates were tabulated in the *Perfumery and Essential Oil Record* (*2*). No range of values is given for the individual essential oils, and therefore the data probably are based on single determinations. The information will prove of some value, especially for labeling and shipping regulations.

Opfer-Schaum and Piristi (*68*) pointed out the little-known fact that musk xylene can exist in three modifications having melting points of 84°, 107°, and 114°; the two melting points of 104° to 106° and 112.5° to 114.5° are often observed by analysts. According to the same investigators, ethyl vanillin is also polymorphous, existing in four crystalline modifications having melting points of 60°, 65°, 74°, and 76°; the commercial product usually shows a melting point of 77° to 78°.

For the evaluation of orange flower water, Deshusses (*23*) recommended the determination of essential oil content; chromic acid oxidation showed the presence of 23 to 26 mg. of oil per 100 ml. of floral water in the samples examined. Using this same technique for rose water, Deshusses (*24*) found 12 to 32 mg. per 100 ml. However, because floral waters contain only small amounts of oil, they are best evaluated by odor and flavor.

For the evaluation of capsaicin and capsaicin-containing drugs and preparations, Büchi and Hippenmeier (*15*) made use of a phosphomolybdic acid reagent with subsequent determination of absorption value in an electrophotometer. In the application of this method to oleoresin capsicum it would appear that the high color of most oleoresins would interfere. North (*66*) developed a colorimetric determination of capsaicin in oleoresin capsicum in which the readily available vanillin is employed for the standard solutions in place of capsaicin.

Euverard and Hurley (*29*) reported a new method for surface tension measurements; the length of an air bubble of given volume in a horizontal tube of known diameter is determined, and from this measurement surface tension values are calculated.

In a review dealing with the structure of alcohols and aldehydes derived from aliphatic terpenes, Naves (*62*) defended the use of the Raman effect for the differentiation of isomeric compounds; other investigators have expressed doubt as to its value for such differentiation.

Crocker and Dillon (*20*) prepared an "odor directory" for 244 aromatic chemicals and 115 natural odorants; this is an attempt to describe odors numerically. It suffers from the basic fallacy of assigning values to a property for which no instrument capable of objective measurement has been conceived as yet. Until objective measurements can be made, such classifications serve no scientific purpose.

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FERTILIZERS

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METHODS of fertilizer analysis published in the period 1943 to 1948 are reviewed in the February 1949 issue of Analytical Chemistry (*78*). The present paper summarizes the subsequent developments in this field and the recent literature—chiefly for 1948—not previously covered. The survey relates not only to procedures that are directly applicable in fertilizer analysis but also to those that are of possible usefulness for this purpose.

SAMPLING AND SAMPLE PREPARATION

Several phases of the problem have been studied by Allen (*2*), who reports that analyses of mixed-fertilizer samples taken with single-tube and double-tube samplers, respectively, were in good agreement. As regards changes in the moisture content of the sample, it appears that double-walled asphalt-impregnated bags made of heavy paper are as satisfactory as glass jars for shipping fertilizer samples from the field to the laboratory. Evidence that there is no need for passing the sample through a 10-mesh screen before grinding the portion for analysis, as specified in the official procedure (*4*, p. 20), is presented.

WATER

Methods for free water in fertilizers have been studied collaboratively by Hill *et al.* (*72*), with special reference to the airflow and vacuum drying procedures. These procedures are of wider application in fertilizer analysis than is oven drying at 100° C.

Caley and Gordon (*25*) describe an improved trap for determination of water by distillation with organic liquids.

NITROGEN

The one hundredth anniversary of the birth of Johan Kjeldahl, who developed the Kjeldahl method for nitrogen which, with its several modifications, has served so well for the determination of this element in fertilizers, was celebrated in 1949 (*173, 186*).

The merit of selenium as a catalyst for the Kjeldahl reaction continues to receive attention. Rauen and Buchka (*134*) present data which indicate that a digesting period of 1 hour after the reaction mixture becomes clear is sufficient when selenium–sulfuric acid mixtures containing 0.7% of selenium dioxide are used, even when lysine and lysine-containing protein are present. According to Mallol (*107*) digestion of organic nitrogen materials to complete decolorization of the solution can be effected in less than 4 minutes by heating the sample with sulfuric acid containing 0.05 gram of selenium per 20 ml. and agitating while concentrated perchloric acid is added dropwise. Bradstreet (*23*) reports that metallic selenium, sodium selenite, and sodium selenate are more effective than the corresponding tellurium products as catalysts for the digestion of aromatic compounds.

On the other hand, Willits *et al.* (*181*) show that there is danger of loss of nitrogen when selenium, alone or with other catalysts, is present in the Kjeldahl digestion of heterocyclic nitrogen ring compounds. The only catalysts necessary with such compounds are mercuric oxide and potassium sulfate, used in the ratio of 0.6 to 15 grams, with 25 ml. of sulfuric acid, and a digestion time of 3 hours. Hiller *et al.* (*73*) also state that mercury is the only catalyst that gives nitrogen values for proteins as high as those obtained by the Dumas combustion method. Detailed procedures given by the latter workers, involving the use of mercury catalysts, include macro- and micromethods with distillation and titration of the ammonia and a micromethod with gasometric determination of the ammonia by the hypobromite reaction.

The results of a comprehensive collaborative study of numerous micro-Kjeldahl procedures for nitrogen are reported by Willits and Ogg (*182*).

Methods for determination of total, water-soluble, and water-insoluble nitrogen and of nitrate and ammoniacal nitrogen in fertilizers are outlined by Nascimento (*118*). The recommended method for total nitrogen involves treatment of the sample with phenolsulfonic acid and sulfuric acid with subsequent addition of powdered zinc, anhydrous sodium sulfate, and metallic mercury, and digestion and distillation in the usual way.

Postnikov and Lapshin (*132*) state that aniline, dimethylaniline, and *o*-toluidine can be used for determining calcium nitride in the presence of calcium cyanamide. Although decomposition of calcium nitride by hot anhydrous ethyl alcohol is only 80% complete in 16 hours, this reaction can be used as the basis of an approximate method for calcium nitride in calcium cyanamide.

That loss of nitrogen may occur when fertilizers containing nitrate and chloride are analyzed by the official Kjeldahl method as modified to include nitrate nitrogen (*4*, pp. 27–28) is further confirmed by White and Ford (*179*) who show that appreciable loss can be expected if the ratio of nitrate ($NaNO_3$) to chloride (KCl) is less than 5 to 2. The loss occurs in the first step of the procedure —the addition of the sulfuric–salicylic acid mixture. In a collaborative study reported by Etheredge (*47*) better results for total nitrogen including nitrate were usually obtained by the Ford modification of the official method than by the Shuey procedure (*152*) or by substituting fuming sulfuric acid for concentrated acid in the official method. For analysis of sodium nitrate the Devarda method (*4*, p. 28) is more rapid and appears to be more accurate than the Ford modification.

Lingane and Pecsok (*101*) describe a method for the determination of nitrate which is based on reduction to ammonium ion by chromous ion in dilute sulfuric acid solution. With amounts of nitrate ion of the order of 20 to 50 mg. the method is precise and is accurate to ±0.2%; with 2 to 5 mg. of nitrate ion the accuracy is about ±2%. Large amounts of chloride do not interfere. Nitrite undergoes the same reduction.

A method for nitrate, described by Holler and Huch (*75*), involves nitrating 3,4-xylenol (3,4-dimethylphenol) in 80% sulfuric acid and steam-distilling the 6-nitro-3,4-xylenol into dilute sodium hydroxide, forming the deeply colored sodium salt which is determined colorimetrically. The recommended concentration range is 0.10 to 0.35 mg. of nitrate nitrogen in 100 ml. of solution, using a cell depth of 1 cm. Interference by chloride and nitrite can be easily avoided by suitable preliminary treatments.

Confirming previous studies (*46*), Etheredge again reports good results by the formaldehyde procedure in a collaborative investigation of methods for nitrogen in ammonium nitrate (*47*). Pieters (*126*) points out that results by this procedure are influenced by the concentration of formaldehyde, the pH, and the duration of the reaction, but the determination can be made under uniform conditions and the titrating solution can be standardized against an ammonium salt of known purity.

Determination of the ammonium ion in fertilizers by conductometric titration with sodium hydroxide is proposed by Jander *et al.* (*81*). Taras (*162*) recommends a 0.1% solution of disodium 4,4′-bis(*m*-tolyltriazeno)-2,2′-stilbenedisulfonate in acetone as an indicator in titrating the ammonia recovered from Kjeldahl distillations by absorption in boric acid. Day and co-workers (*34*) describe an improvement in the microaeration technique of Sobel *et al.* (*154*) for absorbing Kjeldahl ammonia in boric acid.

Developments in equipment for micro-Kjeldahl determinations include apparatus in which the digestion and distillation take place in the same vessel (*11*, *140*), a distillation apparatus (*83*), and a vibrator to prevent bumping in digestions (*70*).

PHOSPHORUS

Mixtures of perchloric and hydrofluoric acids are frequently used to decompose siliceous phosphates, especially products made by high-temperature processes. It is recognized that some loss of phosphorus may occur when phosphatic materials are heated at high temperatures with these acids. Chapman *et al.* (*26*) show that other elements may also be lost. Thus, among those of possible interest to the fertilizer chemist, complete volatilization of boron, silicon, and arsenic and appreciable loss of manganese and chromium occur at 200° C., whereas potassium, sodium, calcium, magnesium, copper, zinc, vanadium, molybdenum, and cobalt are not affected.

For determination of phosphorus in protein-containing substances, decomposition of the sample with concentrated sulfuric acid and Perhydrol is recommended by Hahn (*64*).

Tschirch (*170*) recommends weighing the phosphorus as magnesium ammonium phosphate hexahydrate after treating with acetone and vacuum drying. With the aid of the Chevenard thermobalance (*29*), Duval (*40*) found that complete conversion of magnesium ammonium phosphate to magnesium pyrophosphate—the form in which phosphorus is usually weighed in its gravimetric determination—can be accomplished at 285° C., as compared with the previously reported temperature of 477° C. (*41*).

Sarudi (*144*) outlines an improved method for precipitating and weighing phosphorus as ammonium phosphomolybdate, $(NH_4)_3PO_4.12MoO_3$. It is recommended that the precipitate stand at least 2 hours before filtering on a Gooch crucible with a sintered-glass bottom (No. 2A) and that the precipitate be protected from atmospheric moisture during drying and weighing. Addition of ammonium nitrate or ammonium carbonate to the wash solution prevents formation of a green color when the precipitate is dried at 160° to 180° C. The phosphorus pentoxide conversion factor is 0.0377, which is within 0.3% of the theoretical value. Ammonium phosphomolybdate is stable at 410° C., but ammonia is lost at higher temperatures (*39*, *40*).

According to Bourdon and Cotte (*22*) the fraction of molybdic oxide fixed by ammonium phosphomolybdate is constant at high acidity (5 *N*) and excess molybdate (4 to 7% solution in MoO_3). Scheffer's method for phosphorus (*145*) is entirely satisfactory under these conditions of precipitation.

In the titration of phosphoric acid with sodium hydroxide Dijksman (*37*) reports that the pH at the end point is 4.25 for titration to $H_2PO_4^-$ and 9.1 to 9.2 for titration to HPO_4^{--}. He suggests an alkalimetric method for phosphorus in phosphates containing calcium, aluminum, and iron, which involves removal of the metal ions by means of a cation exchanger (Dusarit).

Determination of phosphorus in monoammonium phosphate by electrometric titration with sodium hydroxide is proposed by Jander *et al.* (*81*). According to Toropova and Yakovleva (*168*), the phosphate ion can be determined successfully under certain conditions by electrometric titration with lead acetate in an atmosphere of hydrogen.

Recently studied colorimetric methods for phosphorus include the well-known molybdenum blue procedure with reduction by stannous chloride (*64*, *110*, *140*), amidol (2,4-diaminophenol-hydrochloride) (*43*), or 1-amino-2-naphthol-4-sulfonic acid (*7*); and the molybdivanadophosphate method (*103*). Studies by Boltz *et al.* (*19*) show that the polarographic waves of molybdiphosphoric acid are considerably influenced by the nature of the supporting electrolyte; two stages of reduction exist, but the half-wave potentials are not well established. Improvements in the isobutyl alcohol procedure for extracting inorganic phosphate from colored solutions (*12*, *129*), with its subsequent determination by the molybdenum blue method, are described by Martin and Doty (*110*). The precipitate formed with molybdivanadophosphate by hydroxyquinoline has the composition $6C_9H_7ON.P_2O_5.V_2O_5.22MoO_3.nH_2O$ (*105*); the complex is soluble in isoamyl alcohol and ethyl alcohol.

Substitution of a pyridine reagent (equal volumes of pyridine and nitric acid) for strychnine in the strychnine-molybdate nephelometric method for phosphorus is proposed by Čupr and Hemala (*33*), who describe a special nephelometer based on measuring the voltage rather than the current from the photoelectric cells.

Guthrie and Nance (*63*) propose a rapid method for direct determination of free phosphoric acid and water-soluble phosphorus in superphosphates, which involves stepwise titration of an aqueous extract of the sample with sodium hydroxide with the aid of suitable indicators.

Cheritat and Vignau (*28*) outline a volumetric molybdate method for total phosphorus in basic slag, which involves decomposing the sample with a mixture of nitric and sulfuric acids, precipitating the ammonium phosphomolybdate without prior removal of the sulfate, and heating on the steam bath. On the basis of previous studies (*79*, *138*, *139*) one would expect this procedure to give high results, owing to interference by the sulfate ion.

Collaborative studies reported by Jacob *et al.* (*80*) show that the present official neutral ammonium citrate method (*4*, pp. 23–24) is a suitable procedure for the evaluation of the phosphorus in basic slag. On the basis of this work the neutral ammonium citrate method was adopted in October 1949 by the Association of Official Agricultural Chemists as the official procedure for "available" phosphorus in basic slag, thus replacing the 2% citric acid method (*4*, p. 25) which had long been used for this purpose. In agreement with other investigators (*71*, *74*, *80*), Barbier and

Trocmé (*8*) show that within certain limits the solubility of basic slag phosphorus in 2% citric acid increases with the fineness of grinding.

Finer grinding of the analytical sample, as with high-speed hammer mills, appears to have only a very small effect on the results for ammonium citrate–insoluble phosphorus in mixed fertilizers (*52*).

Martens (*109*) discusses the solubility of phosphates in water, ammonium citrate, and mineral and organic acids. He concludes that present analytical methods do not permit a quantitative separation and determination of the different calcium phosphates—a fact that is not well recognized in some quarters.

Thus far, synthetic organic phosphorus compounds have found no place in the fertilizer industry. However, such compounds are of potential interest to the fertilizer analyst because of the recent developments in their use as pesticides and the possibility of their inclusion in fertilizer preparations. According to Wreath (*183*), decomposition of the sample by means of the semimicro Parr bomb method yields excellent results on all types of organic phosphorus compounds. Digestion with nitric and perchloric acids, with proper precautions against explosions, is also suitable for such compounds as hexaethyl tetraphosphate, tetraethyl pyrophosphate, and tributyl, tritolyl, and triphenyl phosphate. The difficulty in hydrolyzing such phosphates by means of aqua regia is pointed out by MacIntire *et al.* (*104*), who show that digestion periods of at least 36 hours may be necessary for complete hydrolysis of some of these compounds. Methods for the determination of tetraethyl pyrophosphate are outlined by Hall (*65*) and Wreath and Zickefoose (*184*).

The behavior of synthetic organic phosphates in the soil and their effect on plant growth cannot be foretold by the conventional analytical procedures used for the evaluation of phosphate fertilizers (*104*).

POTASSIUM

Perrin (*124*) has developed a modification of the chloroplatinate method for potassium in fertilizers, which is reported to have a number of advantages over the official procedure (*4*, pp. 31–32). It involves an improved wet combustion with aqua regia to destroy ammonium salts and organic matter, with simultaneous precipitation of the potassium chloroplatinate.

A modification of the perchlorate method, which does not require preliminary removal of sodium, magnesium, ammonium, sulfate, and chloride ions, is described by Lejeune (*97*). The procedure is rapid and is said to be accurate within 2%.

The hexanitrodiphenylamine method of Sheĭntsis (*150*) has been adapted to the determination of potassium in fertilizers (*55*). Prior removal of sulfate, phosphate, and ammonium ions is necessary. The accuracy of the procedure is reported to be as good as that of the chloroplatinate method.

A volumetric method for determination of potassium in mixtures of magnesium and potassium sulfates is based on the use of Gaspar's reagent (2.5 grams of calcium ferrocyanide dodecahydrate dissolved in 500 ml. of water plus 500 ml. of ethyl alcohol, *141*). Potassium in aqueous solution can be determined by precipitating and weighing as the salt of 2-chloro-3-nitrotoluene-5-sulfonic acid (13.5% potassium) (*20*); barium and ammonium salts interfere.

Ford (*52*) reports that finer grinding of the analytical sample, as with high-speed hammer mills, does not generally result in higher values for soluble potassium in mixed fertilizers. On the contrary, somewhat lower values may often be obtained.

For the determination of potassium in siliceous materials Elving and Chao (*45*) have combined hydrofluoric acid decomposition of the sample with a convenient procedure for the removal of calcium and magnesium. The method is said to be accurate and much simpler in manipulative details than the J. Lawrence Smith method. Gaudin and Pannell (*58*) describe a method for the radioactive determination of potassium in minerals, which is applicable to concentrations of potassium above 1%.

Several modifications of the cobaltinitrite method have been developed for the micro- and semimicrodetermination of potassium. They comprise titration of a potassium dichromate solution of the cobaltinitrite precipitate with standard iron solution (*21*); photometric determination of the nitrite as nitrosoindole (*84*); and turbidimetric determination of the cloud formed by a reagent composed of sodium cobaltinitrite, sodium nitrite, methanol, and methylene glycol (*166*).

A rapid and sensitive micromethod for potassium is based on the polarography of the periodate (*156*).

Potassium can be completely separated from sodium by means of an organic ion exchanger (Amberlite IR-100 resin) with the aid of perchloric acid (*87*). Fixation of the ammonia with formaldehyde eliminates its interference in the sodium lead iodide test for potassium (*48*).

Investigations of the flame photometer method for potassium include development of improved apparatus and techniques (*96*, *125*, *178*) and studies of sources of errors and their reduction (*17*, *122*, *148*, *158*, *169*). It appears that satisfactory application of the method to mixed fertilizers has not been achieved.

CALCIUM

In a critical study of the oxalate method for calcium Holth (*76*) found that double precipitation is necessary for accurate analysis, a large excess of ammonium oxalate must be used to avoid precipitation of magnesium from supersaturated solutions, and the solution must be kept 4 hours at room temperature before filtering. For the analysis of phosphate-containing solutions Edwards and Alcock (*42*) remove copper and zinc and precipitate the oxalate in the presence of tartaric acid, with subsequent ignition to the oxide. Tschirch (*170*) gives a procedure for determining calcium by weighing as the oxalate after treating with acetone and vacuum drying. When calcium oxalate is heated, calcium carbonate is the stable product at 420° to 660° C., while conversion to the oxide is complete at 840° C. (*40*).

Methods for the determination of calcium by permanganate titration of the oxalate are outlined by several investigators (*77*, *91*, *161*, *185*). According to Ingols and Murray (*77*), the use of the hydrolysis of urea for raising the pH of a solution containing calcium and oxalate ions permits formation of large, readily filtered crystals of calcium oxalate. These crystals are less contaminated than the small crystals formed by the standard method, and the time required for the determination is reduced as much as 50%. Birnbaum and Shchigol (*18*) propose precipitation of the calcium with standard sodium oxalate and potentiometric titration of the excess oxalate with silver nitrate in ammoniacal solution. Also, calcium can be determined by potentiometric titration of the oxygen-free solution with sodium oxalate in the presence of cadmium chloride and ethyl alcohol (*137*).

Shvedov (*153*) reports that separation of calcium from magnesium by precipitation as calcium sulfate in the presence of acetone has no advantage over the usual oxalate separation.

Gravimetric and titrimetric methods for determining calcium with the ferrocyanide ion are described by Flaschka and Spitzy (*51*). A volumetric method for calcium involves formation of a red solution with ferric chloride and ammonium thiocyanate, and either visual or amperometric titration with sodium fluoride in the presence of ethyl alcohol (*136*, *137*).

Small quantities of calcium can be determined colorimetrically with the aid of picrolonic acid and methylene blue (*89*) or by precipitation as $CaK_2Ni(NO_2)_6$ and estimation of the nickel by the dimethyglyoxime reaction (*171*). The chloranilic acid method has been studied by Gammon and Forbes (*54*) with special reference to the interference of iron and magnesium. Paper chromatography has been extended to the separation, detection, and determination of calcium (*3*).

Other methods for calcium include its determination by the flame photometer (*169*) and by subjective spectrophotometry (*62*). Murexide (*146*) and 5,6-benzoquinaldic acid (*106*) have been investigated as analytical reagents for calcium. In the absence of iron and aluminum, calcium can be separated from magnesium by precipitating the latter as magnesium hydroxide (*61*).

MAGNESIUM

Several studies of the analytical precipitation of magnesium ammonium phosphate and its subsequent treatment are summarized in the section on phosphorus (*40, 41, 170*). To determine magnesium in filtrates from calcium oxalate precipitation, by either the magnesium ammonium phosphate or the oxine (8-hydroxyquinoline) method, Holth (*76*) states that ammonium oxalate must first be removed, preferably by oxidation with bromine or by evaporation of the solution to dryness and heating over a free flame. Hardin and MacIntire (*67*) dissolve the magnesium ammonium phosphate in hydrochloric acid and titrate with sodium hydroxide in the presence of bromocresol green.

Determination of magnesium in materials containing aluminum, iron, calcium, and phosphorus by the oxine method is described by Edwards and Alcock (*42*). Investigations of this method are also reported by Fischinger (*50*) and Have (*68*). The latter's results indicate that 1 ml. of 0.1 *N* potassium bromate is equivalent to 0.486 mg. of magnesium oxide.

Sane and Telang (*143*) and Tananaev (*161*) outline rapid alkalimetric methods for magnesium in limestone and dolomite. Reznik and Fedorova (*135*) propose a phototurbidimetric titration procedure for this determination.

Abrahamczik (*1*) uses acetylacetone for extraction of iron, aluminum, and manganese, which interfere in the Titan yellow colorimetric method for magnesium. Pieters *et al.* (*127*) form the Titan yellow complex in the presence of a glycerol-starch mixture as a protective colloid; they state that aluminum, ferric, orthophosphate, and ammonium ions, silica, and large amounts of alkali ions interfere. Other reagents proposed for the colorimetric determination of magnesium include *p*-nitrobenzeneazoresorcinol (Magneson) (*142*) and diphenylcarbazone (*174*).

An amperometric method for magnesium involves titration in sodium fluoride solution with standard aluminum sulfate in the presence of ferric chloride as an indicator and with addition of ethyl alcohol to double the volume (*137*).

Murexide (*146*), 5,6-benzoquinaldic acid (*106*), and Naphthazon 1 and 2 (*133*) have been investigated as analytical reagents for magnesium. Differential solubility of the sulfites in 50% ethyl alcohol is the basis of a procedure for separating magnesium from calcium, barium, strontium, and lead (*57*).

SULFUR

Duke *et al.* (*38*) have studied the rate of precipitation of barium sulfate with the aid of a high-frequency conductometric titration apparatus. Tannin is more effective than acetic acid in reducing interference by the chromic ion in the barium sulfate procedure (*99, 100*). Interference by aluminum is slight (*98*). A technique for handling barium sulfate precipitates involves treatment with acetone and vacuum drying (*170*). In the method of Freze (*53*) barium sulfate is determined by comparing the densities of a freshly precipitated suspension and its filtrate.

Pchelintsev (*123*) and Soĭbel'man (*155*) describe a volumetric iodometric method for sulfate. For determination of sulfur in gypsum, Vian (*175*) proposes conductometric titration with barium acetate. Benzidine sulfate procedures are reviewed by Thomson (*165*).

BORON

Taylor (*164*) outlines methods for borax in mixed fertilizers which involve dissolving in sodium carbonate solution, removing interfering substances by means of barium chloride and barium carbonate additions to the acidified extract, and titrating with sodium hydroxide in the presence of mannitol. The methods are reasonably accurate and precise and are superior to the A.O.A.C. method for water-soluble boron (*4*, pp. 32–33).

Among 60 organic compounds tested for their suitability as either colorimetric or fluorometric reagents for boron Ellis *et al.* (*44*) choose 1,1′-dianthrimide and 1-amino-4-hydroxyanthraquinone, respectively. A colorimetric method for boron in borate ores is based on the use of carmine red (*88*). Methods for detecting boron include a flame test (*59*) and the use of azo dyes derived from salicylic acid (*90*).

MANGANESE

A modification of the Volhard method for manganese involves both sodium arsenite and potassium permanganate titrations (*15*). In the Volhard-Wolff procedure use of an equivalence value of 1.651 mg. of manganese per milliliter of 0.1 *N* potassium permanganate is reported to give more accurate results than the theoretical value of 1.648 mg. (*56*). Studies have been made of the factors involved in the gravimetric determination of manganese as basic bismuth permanganate (*69*) and as tetraphenyl phosphonium permanganate (*112*).

Nydahl (*120*) and others (*27*) discuss the persulfate method for manganese. It can be used in the presence of the chloride ion and organic matter and is quicker than and at least as accurate as the periodate method. The latter method is discussed by Lacroix and Labalade (*95*).

A gravimetric method for determination of manganese by precipitating with oxine and drying at 160° C. is outlined by Neelakantam (*119*). In a volumetric procedure proposed by Tomíček *et al.* (*167*) manganese is titrated potentiometrically with potassium ferricyanide in the presence of ammonium carbonate and potassium cyanide.

5,6-Benzoquinaldic acid has been investigated as an analytical reagent for manganese (*106*). The element can be detected and determined with the aid of paper chromatography (*3*).

COPPER

Recently proposed gravimetric methods for copper involve its precipitation with isoquinoline (*157*) or *o*-phenylenediamine (*163*). The cuprous oxide procedure is discussed by Tschirch (*170*). Cupric oxide is stable in the temperature range 500° to 946° C. (*39*).

Hammock and Swift (*66*) report that the accuracy of the iodometric method for copper is improved by titration in the presence of potassium thiocyanate. In a modification of the iodometric procedure the copper is precipitated as the arsenate (*147*).

In Krause's method (*92*) copper is determined by precipitating with disodium phosphate from an acetic acid–sodium acetate buffered solution and titrating the excess phosphate with standard zinc solution. Another volumetric method for copper involves its precipitation as cuprous thiocyanate (*24*). Amperometric titration of copper with either oxine (*159*) or potassium ferrocyanide (*30*) has been proposed.

Some recently described colorimetric methods for copper are based on its reactions with sodium diethyldithiocarbamate (*85*), trisodium citrate (*49*), potassium thiocyanate (*115*), and perchloric acid (*10*). A polarographic method for copper makes use of a "regulating solution" containing sodium potassium tartrate and sodium hydroxide (*121*).

Recently investigated analytical reagents for copper are rubeanic acid (*3*), 5,6-benzoquinaldic acid (*106*), and murexide (*146*). The cupric ion can be separated from calcium by taking advantage of the relative solubilities of the sulfites in dilute ethyl alcohol plus ammonium hydroxide (*57*).

ZINC

Gravimetric determination of zinc by precipitation with isoquinoline in the presence of ammonium thiocyanate is proposed by Spakowski and Freiser (*157*). Tschirch (*170*) outlines a gravimetric method for determining zinc as the ammonium phosphate compound which is stable at temperatures of 40° to 150° C. (*39*).

Maun and Swift (*111*) have improved the ferricyanide method for iodometric determination of zinc. The precision of the modified procedure is 1 to 2 parts per thousand. In a colorimetric method zinc is precipitated with diethylaniline and potassium ferricyanide and the iron is determined photometrically (*16*). Popper (*131*) titrates zinc sulfate conductometrically with potassium ferrocyanide.

An indirect potentiometric method involves precipitating the zinc with potassium ethyl xanthate, treating the precipitate with silver nitrate, and titrating the excess nitrate with potassium iodide (*13*). Zinc can be titrated amperometrically with oxine (*159*).

Improvements in the colorimetric dithizone method for zinc have recently been developed (*151, 177*). A paper chromatography method for zinc is based on the dithizone reaction (*3*).

Methyl violet with ammonium or potassium thiocyanate (*94*), 5,6-benzoquinaldic acid (*106*), and murexide (*146*) can serve as analytical reagents for zinc.

COBALT AND MOLYBDENUM

Studies of the factors affecting the colorimetric determination of cobalt with nitroso R salt have been made by several workers (*31, 35; 108*). A spectrophotometric method for cobalt involves its determination as cobaltous chloride in ethyl alcohol solution (*5*). Analytical reagents for cobalt include rubeanic acid (*3*) and 5,6-benzoquinaldic acid (*106*).

According to Barshad (*9*) color development in the thiocyanate-stannous chloride method for molybdenum is considerably enhanced by the presence of ferric and nitrate ions. The quantitative aspects of the intensification were studied. A new method for small quantities of molybdenum is based on its separation by means of cupferron and chloroform and its colorimetric determination with toluene-3,4-dithiol (*128*).

CHLORINE

Berry (*14*) reports that in the Volhard method for chlorine the excess silver can be titrated in the presence of the silver chloride precipitate with good results if tartrazine is used as the indicator instead of a ferric salt. Vorob'ev (*176*) points out sources of error in the Berg method which involves fixation of bromine and iodine ions with acetone and determination of the chlorine by the Volhard method. Crude resorcinol succinein and resorcinol tricarballein can be used as adsorption indicators in argentometric titration of the chloride ion (*113*). Silver nitrate can be replaced in chlorine titrations by mercuric nitrate with sodium nitroprusside as an indicator (*172*).

A coulometric method for chlorine is based on electrolysis of a chloride solution with a silver anode of carefully controlled potential (*102*). Methods for potentiometric titration of chloride with silver nitrate are described by Shchigol (*149*) and Kubli *et al.* (*93*).

FLUORINE

According to Kaufman (*86*) the lower satisfactory limit of the lead chlorofluoride method is 10 to 20 mg. of fluorine. The pH of the precipitation should be 4.6 to 4.7. In a modification of this method the chlorine content of the chlorofluoride precipitate is determined by Volhard's procedure (*130*).

Filtration of calcium fluoride precipitates is aided by the presence of a small amount of gelatin (*180*). In the case of mixtures of calcium fluoride and calcium sulfate, removal of the calcium fluoride from the weighed precipitate by treating with boric and perchloric acids and washing, with subsequent weighing of the residual calcium sulfate, is a convenient indirect way of determining the fluorine.

The well-known and widely used silicon tetrafluoride volatilization method for fluorine has been studied by several workers (*6, 114, 116*). Instead of sodium alizarin sulfonate—the commonly used indicator in the thorium nitrate titration—Milton (*114*) recommends Chrome Azurol S, and Ballczo (*6*) uses a combination of sodium alizarin sulfonate and methylene blue.

A potentiometric method for fluorine involves its titration with ferric chloride (*160*). Formation of a complex with hematoxylin and zirconium nitrate is the basis of a colorimetric method for fluorine (*82*). Moreno Martín (*117*) discusses the ring test for fluorine.

CARBON DIOXIDE AND NEUTRALIZATION VALUE

The Knorr alkalimeter is used by Clark *et al.* (*32*) in a procedure for carbonate carbon in mixed fertilizers. Good results were usually obtained in a collaborative study of the method. Della Gatta (*36*) describes a new calcimeter for determining carbon dioxide. Tananaev (*161*) proposes a "difference" method for carbon dioxide in dolomites.

Geitlin's method for active calcium oxide in lime involves treatment with sodium carbonate and determination of the residual sodium carbonate and the sodium hydroxide by titration of separate aliquots of the solution with the aid of phenolphthalein and methyl orange, respectively (*60*). The results are 1 to 2% too high.

ORGANIC MATTER AND ASH

Clark *et al.* (*32*) propose methods for determining ash-free water-insoluble organic matter and ash in acid-insoluble matter in mixed fertilizers. The method for organic matter involves its separation from the sample with the aid of a calcium chloride solution (specific gravity 1.40) to which are added 4 ml. of concentrated hydrochloric acid per liter. In the method for ash the sample is boiled with hydrochloric acid (1 + 1) and the residue is ignited at 600° C. In a collaborative study of these procedures erratic results were obtained for organic matter, but the figures for ash were generally in good agreement.

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FOOD

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THIS review, covering the period November 1948 to November 1949, is a sequel to a review of methods of food analysis (*95*) which embraced the preceding 5-year period.

MOISTURE

The Karl Fischer reagent has been applied to the determination of moisture in dried egg white, gelatin, gluten, soy protein, zein, feathers, hair, etc. (*83*). Except in the case of casein and peanut kernels, good agreement was observed with values obtained by drying in vacuo over magnesium perchlorate. A rapid (7-minute) method, suitable for plant control work, has been reported for moisture in sweet potato starch and other particulate materials (*4*). The specific gravity of the particles is determined psychometrically in large samples ranging in moisture content from 15 to 50%.

ASH

The conductometric method for the determination of ash has been developed for both white and raw sugars (*50, 51*). It rests on the fact that the per cent ash (resulfated ash less 10%) is directly proportional to the specific conductance (expressed in micromhos). A dipping type conductivity cell is used with a Leeds & Northrup sugar ash bridge. Comparison of conductometric and ashing methods applied to refined lactose has shown (*18*) the former to be much more precise as well as less time-consuming (0.75 *vs.* 17 hours).

CARBOHYDRATES

The applicability to food analysis of the colorimetric methods for reducing sugars so widely used in biochemical and clinical laboratories has again been emphasized in a paper reporting comparison with Munson-Walker values (*36*). The ferricyanide method has been adapted to the determination of lactose and sucrose in dairy products (*60*) but is not applicable in the presence of other reducing sugars. Mixtures of glucose, galactose, and rhamnose have been analyzed in hydrolyzates of the flavonol glycosides of buckwheat by means of Schoorl's copper reduction method (*19*) before and after fermentation by yeasts capable of selective destruction of glucose alone and of glucose and galactose together. Paper chromatography was used for qualitative identification of the sugars (*97*). Paper chromatography of mixtures of simple hexoses and pentoses has been facilitated by the use of two new solvent mixtures, ethyl acetate–acetic acid–water and ethyl acetate–pyridine–water, in which the sugars have a low R_F (*69*).

The effect of commercially available decolorizing carbons on the recovery of dextrose, levulose, and sucrose from aqueous solution has been investigated (*8*). While most of the carbons failed to retain the two hexoses, sucrose recovery varied from 43 to 87%, except in the animal charcoals where it was retained only from very dilute solution. In studies on the reducing sugar content of potatoes it has been found that ion exchange resins (Amberlites IR-100 H-AG and IR-4 B-AG) removed nonsugar reducing substances more effectively than either neutral lead acetate or carbon (*127*).

A rapid plant control method for the determination of degree of inversion of inverted sugar sirups is predicated upon the relation: per cent inversion $= 100(A_s - A_m)/(A_s - A_i)$, where A signifies rotation and the subscripts s, i, and m denote pure sucrose, pure invert sugar, and the mixture, respectively (*98*). Studies of the effect of curing and drying of forage crops on their soluble carbohydrate content have given rise to a rapid method of simultaneous extraction of both sugar and carotene (*120*), which involves disintegration of the plant tissue in a blender with a mixture of ethanol, Skellysolve, and aqueous sodium chloride.

The physical properties of dried milk or whey are influenced by the relative proportions of α- and β-lactose present. A differential method of analysis (*25*) is based upon the addition of an excess of α-lactose hydrate to the sample, determining the solubility at several time intervals, extrapolating to zero time to obtain the initial solubility from which the amount of β-lactose in the mixture is calculated, and the quantity of α-lactose is obtained by difference between total and beta. Conditions have been described for the determination of maltose and glucose in as little as a few milligrams of mixtures by means of the molybdenum blue reaction (*7*). Complete hydrolysis of the maltose without destruction of glucose is effected by autoclaving for 1 hour at 15 pounds' pressure in dilute hydrochloric acid, the colorimetric reaction being conducted before and after hydrolysis. Direct polarimetric determination of the starch content gives results for patent flour in good agreement with conventional methods of nonstarch analysis but 1.3 to 2.6% higher for whole wheat (*26*).

Methods for the differential determination of the linear (amylose) and branched chain (amylopectin) components of starch with avoidance of concomitant degradation continue to be sought by investigators. The features of several previously published methods have been incorporated in a quantitative separation of the two fractions based on their respective solubilities in hot (60°) water and in butanol- or thymol-saturated water (*77*). A practical method for determining the "grade" of pectin—i.e., the ratio of sugar to pectin in a jelly of standard strength—is based on the adoption of a suggested standard for strength (*6*). The breaking point of jelly slices is measured with a calibrated Tarr-Baker gelometer.

FATS

Technologists concerned with the bacteriological examination of edible fats will be interested in the use of an inert emulsifying diluent consisting of an aqueous mixture of 2% by volume of Tween 80 and G-2800 (both from Atlas Powder Company, Wilmington, Del.) (*20*). A microdiffusion technique adapted to the determination of volatile fatty acids (*13*) would seem to have possibilities in the examination of edible fats and oils when the number or quantity of samples precludes steam distillation. A method has been described for estimating the proportion of butterfat, coconut oil, and palm kernel oil in margarine which is based on the relation between their Reichert, Polenske, and Kirschner values (*126*). The applicability of this procedure to American margarines containing such variable types of refined and hydrogenated oils appears to be questionable.

PROTEINS AND AMINO ACIDS

A critical study of conditions for the Kjeldahl determination of nitrogen in proteins has led to the conclusion that mercury is the only catalyst capable of yielding as high values as the Dumas combustion method (*57*). To avoid the ammonia-binding effect of mercuric oxide in alkaline solution, reduction by zinc dust is employed rather than conversion to sulfide. Copper-selenium catalyst in the sulfuric-phosphoric acid digestion is said to give results several per cent lower than the Dumas dry combustion.

The correlation of collagen content with tenderness of meat has provoked interest in its analytical determination. A recent contribution in this direction involves the centrifugal separation of insoluble collagen from a homogenate of beef tissue adjusted to pH 5 (*56*). The procedure is less reproducible in cooked than in raw beef.

A microbiological method for determination of the biological value of intact, unhydrolyzed proteins is based on the acid production of suspensions of the ciliated protozoan *Tetrahymena geleii* H (*103*). After prolonged (41 days') incubation, values were obtained for egg, milk, soybean, yeast, and wheat germ proteins in fair agreement with those found by the classical nitrogen balance procedure.

As the result of a comprehensive critical investigation of the hydrolytic destruction of tryptophan, methods have been evolved for the determination of this amino acid with high degrees of precision and accuracy even in the presence of carbohydrates. The effects of temperature, alkalinity, and other amino acids on the kinetics of the destructive process have been studied. The basic colorimetric reaction involves treatment with *p*-dimethylaminobenzaldehyde in concentrated sulfuric acid followed by oxidation to a blue color with sodium nitrite (*113*). A microadaptation of the colorimetric method of Sullivan and Hess has been described for the estimation of tryptophan in protein and bacteria (*115*). A yellow-green fluorescent compound, resulting from the action at room temperature of perchloric acid in the presence of bichromate, appears to be specific for tryptophan in proteins (*119*). Quantitative application of an earlier form of this test has been described whereby the tryptophan content of unhydrolyzed proteins is determined within ±5% (*54*). The determination of lysine by the color developed with phenol reagent after bromination, although nonspecific, has been adapted to the estimation of this amino acid in the basic fraction separated by Permutit after appropriate correction for interference by histidine (*71*).

Leuconostoc mesenteroides has been employed for the assay of phenylalanine (*64*), leucine (*65*), and isoleucine (*66*) in proteins and foods. In the latter paper, attention is drawn to the impurity of most commercial samples of this amino acid; a sample which gave no change in acid production after repeated recrystallization from dilute alcohol was considered sufficiently pure for use as a standard. A new microbiological assay for proline with *Lactobacillus brevis* has yielded values of 10.5 and 0.57%, respectively, for moisture- and ash-free casein and silk fibroin (*35*). Studies leading to the development of a microbiological assay for alanine (*105*) have indicated *Leuconostoc citrovorum* 8081 to be the preferred organism. The medium contained, inter alia, 17 amino acids and a liver preparation (Reticulogen). D-, L-, and DL-alanine respond equally. Under certain conditions pyridoxal or pyridoxamine interfered.

The usefulness of chromatography in the analytical separation of amino acids continues to gain recognition. The dominant role being played by the English workers in this field is illustrated by the abstracts of a symposium on partition chromatography and its application to biochemical problems (*12*). The papers covered studies of protein structure—i. e., the order of arrangement of amino acids within the protein molecule—and chromatography of carbohydrates, organic acids, purines, pyrimidines, anthocyanins, and flavones.

Further improvements have been reported (*90*) in the fractionation of protein hydrolyzates on starch columns, particularly in respect to the choice of solvent mixtures. Thus 2.5 mg. of a mixture containing 17 amino acids and ammonia were quantitatively fractionated by means of three starch columns, the solvents being 2:1 *n*-propyl alcohol–0.5 *N* hydrochloric acid, 1:2:1 *n*-butyl alcohol–*n*-propyl alcohol–0.1 *N* hydrochloric acid, 2:1:1 *tert*-butyl alcohol–*sec*-butyl alcohol–0.1 *N* hydrochloric acid, and 1:1:0.288 *n*-butyl alcohol–benzyl alcohol–water. In the attempt to place paper chromatography of amino acids on a quantitative basis, various methods have been studied. Promising results have been obtained with polarographic analysis of the amino acids as their copper complexes (*86*). The ratio of the spot areas of chromatograms of two concentrations of an unknown to corresponding areas of the standard is the basis of quantitative paper chromatographic analysis of amino acids (*40, 41*).

VITAMINS

The adoption of a new International Standard for vitamin A (crystalline vitamin A acetate) and the redefinition of the International and U. S. Pharmacopœial unit on a gravimetric basis (one unit equals 0.3 microgram of vitamin A) (*123*) mark great advances in the assay for this vitamin. Added to this is the official acceptance for the forthcoming U. S. Pharmacopœia XIV of the spectrophotometric assay for vitamin A to replace the present biological assay (*124*). Much of the confusion associated with conversion of spectrophotometric absorbancies to biological units (*37*) should now vanish. The new assay of U.S.P. vitamin A-containing products provides for the measurement of the absorbancy of the unsaponifiable extract at 310, 325, and 334 mμ and the use of the Morton-Stubbs calculation (*92*) to correct for irrelevant absorption. A nomogram has been proposed to facilitate this computation (*96*). To provide assurance of specificity of the spectrophotometric assay, the U.S.P. monographs for vitamin A products will require an "identification test" whereby the ratio of the value obtained in a colorimetric (antimony trichloride) test to that obtained by the spectrophotometric assay must fall within the limits 1.00 to 1.30.

Although this assay is suitable for pharmaceutical oils and preparations and for animal feeding oils and concentrates, it is not adaptable in its present form to the assay of foods and feeds. For this purpose chromatographic and colorimetric procedures have been and are being developed. In a method for the assay of whale liver oil (*55*) which shows promise of wider application, a petroleum ether solution of the unsaponifiable extract is chromatographed on a column of alumina especially treated to weaken its absorbing capacity. Elution is effected with mixtures of petroleum ether containing gradually increasing proportions of ethyl ether. Spot tests with antimony trichloride serve as the indicator for the collection of appropriate fractions which are then measured spectrophotometrically. Improvement of the adsorption step in the assay of mixed feeds for vitamin A has been effected by substituting a mixture of activated magnesia and diatomaceous earth (Hyflo Super-Cel) for sodium carbonate previously suggested by the same group of workers (*27*). In the determination of vitamin A esters no interference is encountered from lycopene and carotene, but the latter is not readily separable from vitamin A alcohol by this procedure. A collaborative study of methods for vitamin A in feeds has been reported (*106*) in which critical, statistical analysis showed fair agreement among laboratories, but the need for continued study was indicated.

Analyses of a sample of dehydrated alfalfa leaf meal for carotene by four variations of the photometric method yielded values by a modified A.O.A.C. procedure significantly higher than by the Wall and Kelley (*125*) or other methods; the differences were attributed to variations in the extraction step (*32*). The superiority of a mixture of cold petroleum ether, acetone (50:50), and quinol (1%), as an extractant for carotene over hot (85°) petroleum alone has been verified (*16*). The latter, while effective for dried grass meal, is only partially so for fresh green leaves unless they are ground to a fine pulp, which has the disadvantage of inducing oxidation. However, an antioxidant can be used during this stage to prevent oxidative loss. A simple extraction and recrystallization method has been reported for the isolation of lycopene for use as a standard in spectrophotometric control of color of tomato products, of which it is the principal pigment (*31*).

Conditions have been developed for the chromatographic separation of the stereoisomers of β-carotene on hydrated-lime columns (*9*). The individual fractions are analyzed colorimetrically. Applying this procedure to alfalfa, it has been found that fully one half of the β-carotenes consist of neo-β-carotenes B and U which have so much lower vitamin A potency than all-trans β-carotene that, unless allowance is made for their presence, estimates of vitamin A potency may be 30% high (*10*).

A beginning has been made in the application of paper chromatography to the resolution of vitamin A alcohol, esters, anhydrovitamin A, and similar chromogens. By means of Whatman No. 54 paper impregnated with hydrated alumina (prepared by successive dipping in aluminum sulfate solution and ammonia) separation has been effected with light petroleum (80° to 100°) in an inert atmosphere (*29*). The Carr-Price reagent has been employed to develop the color, Sudan yellow and Sudan red being employed as indicators of the activity of the paper. In the author's laboratory low-intensity ultraviolet radiation has proved helpful in revealing the fractions by their fluorescence (*15*).

Announcement has been made of the adoption by the Expert Committee on Biological Standardization of the World Health Organization of the new international standard for vitamin D, the unit being the activity of 0.025 microgram of vitamin D_3 (*93*). Relative to assays conducted with the present U.S.P. reference cod liver oil, U.S.P. (rat) assays using the new standard will average 6.4% lower, whereas A.O.A.C. (chick) assays will average 25% lower—i.e., 4 A.O.A.C. chick units equal 3 International chick units of vitamin D. The date of availability of the new standard is not known at the present writing (December 1949).

A chemical procedure for determining the content of the tocopherols in foods has been described and data have been presented to demonstrate its applicability to vegetables, cereals, and other low-fat foods (*100*). The method provides for measuring total, γ-, and ϑ-tocopherols; α-tocopherol is computed by difference, since the β- compound has been found only in wheat germ oil. The steps in the analysis involve freezing and dehydration of the sample, homogenization, extraction of the lipide fraction, molecular distillation of the extract, hydrogenation to eliminate interference by carotenoids, and finally colorimetric analysis by a modified Emmerie-Engel technique. Multiple-unit apparatus for extraction and for semimicromolecular distillation are described. From the same laboratories has come an adaptation of this procedure for foods high in fat and low in tocopherol—e.g., animal tissues (*99*). The changes deal chiefly with the methods of sampling, homogenization, and extraction.

A modification of the original *Lactobacillus fermenti* method for thiamine is based on assays before and after sulfite treatment, standard tubes being supplemented with the sulfite-treated extract to equalize the effect of nonspecific inhibitory or stimulatory substances (*42*).

A synthetic cation exchange resin (KH-9) with *p*- and *o*-phenolsulfonic acids as its base has been proposed as superior to activated zeolite for the adsorption of riboflavin (*48*). Its use is suggested also in the determination of pyridoxine and nicotinic acid. Another fluorometric method has been described for the estimation of riboflavin, which is claimed to avoid the necessity for adsorption (*75*). Interference by nonspecific reducing substances is lessened by washing the extracts with chloroform and subsequent potassium permanganate oxidation.

An addition has been made to the list of aromatic amines suggested for the chemical estimation of nicotinic acid—viz., *p*-aminopropiophenone (*73*). Careful temperature control and timing of the colorimetric readings appear to be essential according to the description of the procedure. This report stresses the need for a complete set of blanks to eliminate discrepancies between chemical and microbiological assays of foods. Nonspecific interference in the fluorometric determination of nicotinamide is claimed to be eliminated in a recent method involving reaction with cyanogen bromide at alkaline pH without recourse to solvent extraction of the fluorescent compound (*23*). Estimation of free and bound nicotinamide is possible. It is of interest to note that nicotinamide could not be detected in bran by this method even after digestion (*76*), indicating that the precursor of nicotinic acid in bran is the free acid rather than the amide. Emphasis is placed on the use of sufficient blanks in the chemical determination of nicotinic acid in cereals in order to avoid the interference responsible for the discrepancy between chemical and microbiological assays (*74*).

Factors affecting the *Neurospora sitophila* assay for vitamin B_6 have been studied (*91*). Interference by thiamine is eliminated by alkaline heat treatment under conditions which leave pyridoxine, pyridoxal, and pyridoxamine relatively unchanged.

Differences have been reported for conjugated folic acid values in yeast, depending on whether hog kidney or chick pancreas was used as the source of the conjugase (*114*). Variably higher values were obtained in yeast as well as in other foods when both enzyme preparations were used successively. Extensive collaborative study of folic acid assays have revealed that satisfactory results may be obtained with either *Lactobacillus casei* or *Streptococcus faecalis* (*43*). The former, being more sensitive, permits diluting out the effect of interfering substances but requires more time and a more complex medium than *S. faecalis*. Chick assays give somewhat higher values than those obtained microbiologically.

Although milk is recognized as a poor source of folic acid, a critical study of methods suggests that failure of various microbiological and chick assays to agree may be due to the presence of variable concentrations of compounds which inhibit or synergize the growth responses (*61*). A fluorescent compound (2-amino-4-hydroxypteridine-6-carboxylic acid) produced by permanganate oxidation is the basis for a chemical method for folic acid (*2*). When interfering pigments (which include oxidation products of tyrosine and tryptophan) are present, the fluorescent oxidation product may be isolated chromatographically. Values reported for a few natural food extracts appear to be somewhat higher than microbiological assays but are possibly within the analytical error of the two methods. Reduction of folic acid with titanous chloride yields an aryl amine which can be diazotized and coupled with the Bratton-Marshall reagent for colorimetric reading at 555 mμ (*52*). Polarography has been invoked in the determination of folic acid in pharmaceutical tablets (*84*), solution of the sample being effected in tetramethyl ammonium hydroxide containing cadmium chloride as an internal standard. The presence of iron causes erroneously high results.

The multiplicity of compounds possessing microbiological vitamin B_{12} activity has been demonstrated on paper chromatograms applied to seeded agar plates producing so-called bioautographs (*128*). Zones of growth are attributed to five desoxyribosides (*111*); crystalline vitamin B_{12} itself has been resolved into two discrete zones using *n*-butyl alcohol–acetic acid as the developing solvent (*129*). The order of magnitude of the potency of the desoxyribosides is only 1/3000 or less than that of vitamin B_{12}; the presence of significantly high concentrations in certain natural products seems unlikely but should not be entirely ignored. Aside from chromatographic separation, it has been proposed that differentiation be effected by assays before and after heating in 0.2 *N* sodium hydroxide in which the desoxyribosides are claimed to be stable, in contrast with the vitamin itself (*63*).

Comparative study of various microbiological assays for vitamin B_{12} is currently in progress under the auspices of the U. S. Pharmacopoeia Anti-Anemia Board. *Lactobacillus leichmannii*, ATCC 7830 (*62, 128*) and 4797 (*110*), and *Lactobacillus lactis* Dorner, ATCC 8000 (*22*), are the organisms currently finding favor, but *Escherichia coli* and *Euglena gracilis* are also used in some quarters. The inhibitory effects of air and oxidizing agents are factors requiring control, at least in the *Lactobacillus* assays. To avoid the variable influence of inhibitory and stimulatory contaminants in tomato juice eluates which were included in certain of the earlier media in the LLD assay, the substitution of fumaric acid and sodium ethoxalacetate has recently been proposed (*22*). Many workers, however, have preferred to replace tomato juice with a pancreatic digest of casein and more recently an asparagus juice concentrate has been used for this purpose (*63*). Care must be exercised in autoclaving the media prior to inoculation with the microorganism, because the purpose is not merely to sterilize but to produce a glucose decomposition product which stimulates initial growth. During this process the presence of a reducing agent such as thioglycollic or thiomalic acid is necessary to protect the vitamin from destruction (*63*). Most of the proteolytic enzyme preparations have proved ineffective for releasing bound vitamin B_{12}; however, digestion with certain fungal proteases—e.g., Prolase B (Wallerstein Laboratories) and Protease 15 (Rohm & Haas)—has resulted in moderate increases in microbiological activity, the significance of which in nutrition is not known.

Agar plate paper disk assays (*49*) have been adapted to vitamin B_{12} in the author's laboratory, and a cup plate assay (*3*) of the type previously reported for other vitamins and amino acids has been developed for vitamin B_{12} (*44*). Twice the precision of the titrimetric tube assay has been claimed for this procedure.

Biological assays for animal protein factor are described which involve the use of mice born of mothers maintained on a depleted diet or of mice whose diets are supplemented with thyrotoxic materials (*17*). These studies indicate the presence in liver of an unidentified factor or factors essential for growth but not present in yeast or wheat germ. A rat assay for "a growth factor" (vitamin B_{12} activity) in liver extracts (*102*) is based on a 2-week depletion followed by a 2-week assay period. The basal ration is essentially a vitamin- and mineral-supplemented mixture of ground yellow corn, soybean meal, and corn oil plus 0.06% iodinated casein. Tenfold variations in the rat potency per U.S.P. unit of antipernicious anemia activity were observed by this method.

The 2,4-dinitrophenylhydrazine method for the determination of diketogulonic, dehydroascorbic, and ascorbic acids, when present together (*104*), has been applied to the analysis of fresh and processed foods (*89*). Most fresh foods contained principally (95% or more) reduced ascorbic acid whereas frozen, canned, and especially dehydrated foods contained more of the oxidation products. It will be recalled that the dehydro acid is biologically active whereas diketogulonic acid is not.

METALLIC IONS

A fluorometric method for aluminum as the γ-hydroxyquinolinate has been described with particular reference to the determination of traces in beer (*121*). The reaction appears to be highly specific and capable of measuring as little as 0.01 p.p.m. of aluminum in beer. In the determination of bismuth, interference from anions which form complexes with this element is avoided by direct quantitative extraction with dithizone in the presence of alkaline ammonium citrate (*67*) or of strong acetic acid (*78*). Phosphates and halides are reported not to interfere under these conditions. Improvements in the dithizone method for traces of cadmium have been effected (*108*) by removal of copper and mercury by carbon tetrachloride extraction and of most of the cobalt and nickel as dithizonates from acid aqueous solution; any remaining cobalt and nickel are removed by adding dimethylglyoxime and extracting with chloroform. The aqueous phase is made alkaline and the cadmium extract is measured as the dithizonate in carbon tetrachloride. The procedure has been applied to dried leafy foods, liver, fruit juices, and excreta. For the determination of reduced metallic iron in enriched cereal foods, a magnetic flotation method has been described for the physical separation of the iron (*94*).

The widespread use of low-sodium diets in the treatment of cardiovascular disease has prompted the determination of the sodium and potassium content in some 500 foods and 150 public water supplies (*11*). The flame photometer was utilized in this survey. In those foods for which comparable data were found in McCance and Widdowson tables (*82*), the latter values were considerably higher, especially in low-sodium foods.

COLOR, ODOR, AND TASTE

Objective evaluation of the color of opaque foods can be effected by means of a photoelectric reflectometer. A method has been described employing the standard Munsell notations, and data obtained on unclarified fruit juices are presented (*132*).

In measuring the color of aged dried milk product it is necessary to extract the brown pigment without loss by adsorption on protein. Preliminary tryptic digestion has been recommended to avoid such loss, the color being read in a trichloroacetic acid filtrate of the hydrolyzed mixture against an arbitrary standard solution of iodine in potassium iodide (*24*).

A committee of the American Association of Cereal Chemists has reported a practical method of evaluating the color of dried eggs, based on the comparison of an ammoniacal water-acetone solution of the eggs with a potassium dichromate standard (0.02% in 1.5 *M* phosphoric acid) (*28*). A "color index" of 100 is defined as the equivalent of 4 mg. of potassium dichromate per gram.

The use of carbon black as an adulterant in chocolate has given rise to a method for its detection and determination involving nitration, acetylation, solvent washing, and ultimate gravimetric estimation by loss on ignition (*109*).

Spectrophotometric data are reported for various certifiable coal-tar colors (*33, 46, 47, 107, 116*).

To the extent that volatile reducing substances in foods are correlated with odor, or more particularly odor intensity, the method of aspiration into standard potassium permanganate solution may be "a useful tool for odorimetry or osphresiometry" (*38*). Data showing losses on aging of various foods such as coffee, spices, and onions have been presented. (Previously the method was applied to the study of fish spoilage.) This procedure ignores qualitative variations, but it may nevertheless have application in certain cases where interest centers in the intensity factor.

Provocative and useful papers on the application of modern statistical methods to food problems have appeared in the recent British literature (*1, 14, 39, 117*). Especially interesting to those concerned with organoleptic evaluation of foods is a recent discussion of statistical designs and interpretation in which, incidentally, attention is drawn to the fallacy of combining ratings of different qualities into a common "score" (*130*).

SPOILAGE

The determination of water-insoluble fatty acids originally proposed for cream and butter as an index of improper spontaneous souring (*59*) has been adapted to dried eggs as a means of detecting souring before drying (*58*). The presence of succinic acid has also been shown to be evidence of decomposition of eggs prior to freezing or drying (*79*). A rapid screening test for detecting fat oxidation in milk powders is based on the addition of a drop of NADI reagent (dimethyl-*p*-phenylenediamine hydrochloride plus 1-naphthol in aqueous acetone) used to detect cytochrome oxidase. A blue color forms in oxidized and tallowy powders roughly proportional to the degree of oxidation (*34*).

CHEMICAL RESIDUES

The chemist concerned with the toxicological examination of foods will find much of interest and value in a systematic procedure recently reported from the New York City Department of Health (*53*). The more common chemical poisons which have been found in foods are classified as volatile, metallic, alkaloidal, and nonalkaloidal and sensitive procedures for their detection are outlined. Emphasis is placed on the importance of a knowledge of history, symptoms, and organoleptic properties in the analytical attack on foods alleged to have caused toxicity. This problem will doubtless become far more complex with the ever-increasing use of newer pesticides for which analytical procedures are not so readily available.

Methods have been developed for the determination of DDT as spray residue on foods (*21*). A procedure applicable to strip solutions of fruits, vegetables, and forage crops where the spray history of the material is known is based on determination of total inorganic chlorine by the sodium and isopropyl alcohol method; a procedure, recommended as a confirmatory test where only small amounts of DDT are present, is based on nitration and development of a blue color with sodium methylate. A spectrophotometric method for determining benzene hexachloride is based upon alkaline hydrolysis and measurement of the ultraviolet absorbancy (at 286 mμ) of 1,2,4-trichlorobenzene which is characteristically different from that of other trichlorobenzenes formed (*30*). The procedure has been applied to animal rations, foods, and biological tissues and with certain modifications to milk (*45*). The high sensitivity of this method—e.g., 0.5 p.p.m. in a 200-ml. sample of milk—and food recoveries augur well for its general acceptance. A microanalytical method for detecting traces of the rodenticide monofluoroacetic acid (1080) in foods is based upon the fluorine content of an isolated organic acid fraction (*101*). To complete the separation of monofluoroacetic acid from inorganic acids which might contain fluorine, use is made of paper chromatography, thus permitting quantitative determinations in the presence of as much as a 1000-fold excess of inorganic fluorine. Total and free sulfur dioxide contents of wines have been determined by a rapid method based upon distillation into dilute lead acetate; optical density of the colloidal suspension of lead sulfite is read photometrically (*88*).

The incorporation of certain sulfa compounds in commercial poultry feeds has prompted the development of methods for their determination. Whereas dilute acid is used to extract sulfaguanidine, an alkaline extraction is employed in the case of sulfaquinoxaline. An adaptation of the procedure of Bratton and Marshall is used in the colorimetric reaction (*122*).

MISCELLANEOUS

A statistical approach to the estimation of the proportion of an ingredient in a mixed food product (*118*) rests upon the relation between the optimum combination of two or more chemical constituents—e.g., soluble solids, free acids, sugar—of an ingredient of the sample and the mean value for the ingredient. The method is said to be applicable to all food products "where the whole of the values of the chemical constituents determined are contributed by the ingredient estimated." Application to the analysis of fruit in jams is discussed.

A new fluorometric method for the estimation of citric acid, applicable to fruit juices, is claimed to require only 4 hours for completion as compared with 24 hours for the standard pentabromoacetone gravimetric method (*80*). It depends upon conversion under anhydrous conditions to aconityl chloride and ultimately to the blue fluorescent compound ammonium citrazinate. Tartaric and malic acids do not interfere but sulfate ion does.

The presence of grape wine in other fruit wines can be detected by a sensitive test for tartaric acid, which has been shown to occur only in products derived from the juice of the grape (*87*). The reaction is based on selective oxidation by periodic acid on α,β-glycols which converts tartaric to glyoxylic acid. This is followed by conversion to a *p*-nitrophenylhydrazone which in alkaline solution yields an intense red compound. A short procedure for the estimation of peroxidase in plant tissues is based on the oxidation of leuco-2,6-dichlorobenzenone-indo-3′-chlorophenol in the presence of hydrogen peroxide, the rate of color formation being proportional to the enzyme concentration (*112*). The leuco dye is claimed to be more sensitive than pyrogallol or leucomalachite green; however, with certain plant materials of low peroxidase and high "dye oxidase" activity, control determinations without peroxide are necessary. In this connection reference is made to the report of the associate referee of the Association of Official Agricultural Chemists reviewing the procedures in current use for the measurement of peroxidase activity in frozen vegetables (*70*).

A proximate method for the detection and estimation of eggs in noodles and similar pastes (*72*) utilizes the content of soluble nitrogen compounds precipitated by ethanol (*a*) and the nitrogen compounds soluble in ammoniacal ether (*b*) as indexes. The ranges for (*a*) in pastes containing 0 to 5 eggs per kilogram of semolina were 0.2 to 0.35 and 1.4 to 1.7%, respectively, whereas the ranges for (*b*) were 0.9 to 1.5 and 3.9 to 4.3%, respectively. Soy flour to the extent of 20% did not contribute significantly to either factor.

Taking advantage of the characteristic ultraviolet absorption of caffeine at 272 mμ, a rapid spectrophotometric method for its determination in coffee and crude caffeine has been developed (*68*). Interfering impurities such as chlorogenic acid and trigonelline are removed by treatment with heavy magnesium oxide and zinc ferrocyanide; in the case of green, roasted, and soluble coffees, oxidation with potassium permanganate is also necessary. Results are reported in good agreement with the official Bailey-Andrew method.

Microbiological methods have been described for the assay of the purines adenine (*5*), cytidine, and uridine (*81*), whereas a microcolorimetric procedure has been reported for thymine (*131*). An interesting photographic technique has been described for revealing paper chromatograms of purine and pyrimidine bases, nucleosides, and related substances, which may have broader application (*85*). It is based upon the detection of the spots on a print made by passing filtered ultraviolet radiation through the chromatogram (the "negative") held in contact with photographic paper.

CONCLUSIONS

It has not been possible in the space available to cover every contribution to the field of food analysis made during the past year; to those investigators whose work may have been overlooked, the author expresses his regrets. In conclusion, special attention of food analysts is directed to the many reports of referees of the Association of Official Agricultural Chemists which appear in the journal of that organization.

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SOLID AND GASEOUS FUELS

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THIS review of the analysis of solid and gaseous fuels is a continuation of the review by Gauger and Darby (*37*) and includes a bibliography of references found from August 1948 through September 1949. The arrangement follows closely that of the original review.

SOLID FUELS

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

SAMPLING

Manning (*64*) shows that the accuracy with which a sample of coal represents the bulk can be calculated from the weight of the sample taken, the particle-size distribution, and the results of the float-sink test. His theory is developed from the calculated distribution of samples drawn at random from a mixture of two different kinds of particles and extended to ternary mixtures. Essential formulas are given and typical examples are worked out.

Bailey and Landry (*3*) discuss sampling of coal for float-sink tests.

PROXIMATE ANALYSIS

Moisture. Cooper, Tarpley, and Abernethy (*16*) have compared the results for moisture as determined in the Brabender semiautomatic tester with those obtained by the standard A.S.T.M. method and found that the Brabender moisture values for 60-mesh anthracite coal ranged from 0.10 to 0.55% higher than those by the A.S.T.M. method; the former method gave results that were 0.05 to 0.15% higher for 20-mesh anthracite. The average difference between the two methods for other ranks of coal, except lignite, was well within the tolerances allowed between different laboratories. Lower values, ranging from 0.10 to 0.30%, were obtained for lignite with the Brabender tester.

Ohlsson (*73*) finds that there is no exact comparison of moisture content of coals possible unless the same method of moisture determination is used in each case. With an American steam coal, used in his tests, lower moisture values were secured on heating at 105° C. for 48 hours than on heating for 24 hours, presumably owing to oxidation. When the heated coals were extracted with xylene, the residual moisture content was higher for the 48-hour heating. Even when this moisture was added, the total moisture was approximately 0.3% lower than that determined by direct extraction of the unheated coal with xylene. In addition, some coals after heating in the moisture-content test are more hygroscopic than calcium chloride and tend to absorb water when cooled in the desiccator.

Bainbridge *et al.* (*4*), having found the British Standard Specification 1016 (1942) method and apparatus for distilling water from a 2-pound sample of coal by use of a petroleum distillate to be very lengthy when used for a brown coal with a high moisture content, developed a method and apparatus which greatly reduce the time, are equally precise with the British standard apparatus, and are more pleasant to work with.

Mielecki (*68*) determines the moisture in peat or brown coal, ground to less than 1-mm. particle size, by placing a 100-gram sample in a flask with 200 ml. of denatured alcohol; the whole is shaken for 5 minutes and left to stand 30 ± 1 minutes. The liquid is then poured into a cylinder, the temperature adjusted to 20° C., and the density measured. The total moisture is calculated from the approximate equation, $\% \text{ moisture} = 974 \times d^{20} - 794.3$, or is read from a chart based on this equation. The maximum error is claimed to be ±5%.

Volatile Matter. Hamaker (*42*) shows that the determination of the volatile content of a coal (exclusive of its water) yields a first indication of the type to which it belongs. However, allowance must be made for the mineral matter present, which may in part be lost through reaction and evaporation during analysis. By using a carbon tetrachloride–benzene mixture of 1.4 specific gravity in a Kattwinkel device, a fraction of low ash content was removed from the coal and analyzed. The uniform calorific value and organic sulfur content on a dry mineral-free basis indicated that this procedure did not affect the petrographic homogeneity.

The method is recommended wherever the volatile content serves as a basis for classification, especially when the sample lies near the borderline between two classes.

Ash. Siniramed (*97*) reports that the rate and duration of heating and the size of sample had no effect upon the determination of the ash content of Sulcis coals.

Thornton (*103*) gives the following as a rapid method of determination of the ash content of coal:

> A representative sample (50 pounds of 1-inch coal) is collected and crushed to 0.5 inch, the sample is reduced to 10 pounds by quartering, and about a dozen increments are used to collect a little over 1 pound. If necessary, this is dried to remove surface moisture and freed from dust over a 20-mesh sieve. One pound is then weighed out and is fed gradually into a special sample jar filled with carbon tetrachloride. When the solution becomes clear, the volume of sink is read off from a scale on the narrow part of the jar. The approximate ash percentage equals 100 times the volume of sink, divided by the weight of sample (grams). The greatest deviation in ash content as compared with the exact method is about 3%. The complete test requires 30 to 40 minutes for a coal that does not require drying.

Hancock (*44*) gives a method for the determination of the ash content based on the specific gravity of coal.

> A gross sample of coal is taken in about 25 increments of 2 pounds each. A steel drum is filled with an amount of water somewhat more than sufficient to cover the amount of coal, and a wire is fixed so as just to touch the surface of the water. The drum and water are then weighed and the coal is weighed separately. Most of the water is then dumped from the drum, the coal is placed in the drum, and the water level is restored so that it just touches the wire. The drum containing water and coal is weighed again, and the specific gravity of the coal is calculated. The per cent ash is then calculated from the equation, % ash = 75 (specific gravity of sample, 1.2). Two gross samples should agree closely if sampling has been adequate. Coals of high moisture content should be air-dried before weighing.

Ash Softening Temperature. Rousseau (*91*) studied and reviews the principal phenomena which take place during the combustion of coal in a grate furnace and in a pulverized-coal furnace.

> Coal was incinerated to constant weight at not over 750° C. Determination of the loss on ignition of the ash thus obtained at various temperatures showed but slight loss (less than 1%) up to 1000° C. At 1300° C. the loss was 4.5 to 17%, the greater losses being obtained with ashes with higher calcium sulfate contents. For the determination of the composition and fusibility of the ash, the coal can be incinerated at 900° C. without introducing a significant error; if only the fusibility of the ash is to be determined incineration can be carried out at 950° C.
>
> In laboratory tests the presence of unburned coal did not significantly affect the fusibility of the ash in either oxidizing or reducing atmosphere. The fusibility of the ash in oxidizing atmosphere was not affected by the addition of 5 to 15% pulverized coke. In the fusibility tests the carbonaceous particles at the outside of the cone burned with formation of carbon dioxide, while those in the inside burned but slightly or not at all and, therefore, did not create a reducing atmosphere capable of converting ferric to ferrous iron. In cones prepared with 10% and especially with 15% coke, there sometimes remained a central carbonaceous core which prevented the cone from collapsing under its own weight. It is certainly a similar phenomenon that gives rise to the formation of unburned particles in the ash obtained in grate furnaces. These results cannot be transposed to industrial conditions without further investigation.
>
> Using two furnaces (horizontal and vertical), Rousseau determined the fusibility of ashes in a reducing atmosphere, obtained by placing a sufficient quantity of coke or semicoke fragments around the test cone, to be lowered by 40° to 140° below the temperature of incipient clinkering and the temperature of 50% reduction in height of the cone is lowered by 10° to 150°; some ashes show an even greater difference. The already numerous fusibility tests do not permit the establishment of any law of refractoriness of the ash on the basis of its composition.

Calorific Value. Edwards (*31*) continues his review of the literature on methods. Calorific value is discussed with inclusion of thirteen recent formulas for calculating the calorific value from ultimate analysis. Methods on specific inorganic constituents are included in eight references. Under assessment of mineral matter of coals for purposes of coal classification fourteen references are reviews (with inclusion of earlier works). Twelve mineral matter formulas are compared.

Rakovshiĭ and Kovalenko (*83*) discuss various formulas relating to the calorific value of solid fuels with their elementary composition.

ULTIMATE ANALYSIS

Carbon and Hydrogen. Babaev (*2*) criticizes the carbon dioxide bulb design (used in Russia) on the ground of entrapped bubble formation owing to faulty shaping of glass parts and improper valve seating. The apparatus for gasometric determination of carbon dioxide is improved by the addition of a second stopcock which permits isolation of the furnace from the gas buret and the atmosphere during absorption of the products of combustion during the first ignition. This design permits accurate analysis of samples containing up to 30% carbon in 0.5-gram samples.

Zhukovskaya (*109*) suggests a new method for the determination of hydrogen in a solid fuel by combustion in a bomb calorimeter.

> On the bottom of the bomb is placed a porcelain dish provided with two wires by which it can be removed. The dish contains 7 to 8 grams of pumice (a layer 3 to 4 mm. thick) which has been saturated by boiling in concentrated sulfuric acid and which serves to absorb the water. When the coal has a high ash content the dish is provided with a cover. A blank run gives the loss in weight of the dish alone without fuel, which must be taken into consideration. When not in use the bomb is kept dry by packing with the pumice absorbent.

Bennett (*9*), in the determination of carbon and hydrogen, bubbles nitrogen through a wash bottle containing 50 ml. of hydrogen peroxide and a few pieces of platinum wire, passes the gas through a flowmeter, a U-tube containing Ascarite and Anhydrone, and thence into the side arm of a silica microcombustion tube containing an asbestos plug, followed by 180 mm. of reduced copper and finally 150 mm. of copper oxide. The platinum catalyzes the evolution of oxygen from the peroxide and the use of reduced copper makes it unnecessary to use lead peroxide. From 2 to 5 mg. of sample are weighed into a boat and burned by the normal Pregl technique.

Nitrogen. Bencze (*8*) describes the details for carrying out a Kjeldahl determination of nitrogen in organic materials. The distilling apparatus consists of a small flask which is shaped something like a retort and contains three essential parts. In one part the liquid ammonium hydrogen sulfate and acid are placed, in another the alkali hydroxide solution, and the last part serves for the absorption of the ammonia gas. This third part is removable and the final titration can be made in it.

Johanson (*50*) describes a micro-Kjeldahl distillation apparatus that is a modification of a type designed by Parnas (*75, 76*) and can be made by the ordinary glass blower. Construction details are given. The outer jacket serves as a vacuum trap for collection of spent sample; construction is simple, with only one internal seal; the whole unit can be held on a single retort stand; there is no loss of ammonia gas; and spent liquor is automatically emptied out on completion of a determination.

Sulfur. Guérin and Moreau (*41*) find that the Eschka method is applicable to high-sulfur fuels, provided care is taken to avoid sulfur losses by very slow heating at the start (1.5 to 2 hours at 250° C.), followed by increase to 800° C. in about 1.5 hours.

Hamaker (*43*) reports that the Eschka method of determination of sulfur in solid fuels gives reproducible results and also possesses the advantage of using apparatus in general use in most laboratories.

Oxygen. Duffy (*28*) presents a nomograph for calculating the total oxygen in bituminous coal from data obtained in the proximate analysis and the carbon content of the coal.

Germanium. Simek *et al.* (*95*) determined the germanium content of the various coals of the Ostrava-Karvina Basin by fusion of the ash with sodium carbonate, dissolving the melt in hydrochloric acid, and distilling off germanium chloride in a stream of chlorine gas. The ash of certain high-volatile coals contained 10^{-6} part of germanium. There is no connection between germanium concentration and the location of the seams. Germanium apparently has no effect on utilization of the coal.

Phosphorus. Klimovskaya (*53*) has separated phosphorus from its various combinations in coal samples.

> Phosphorus which is bound to calcium is separated by extraction with citric acid; the method is similar to that used in fertilizer and soil analysis. The phosphorus combined with magnesium is obtained by treatment of the residue with 10% methanol for 24 hours at room temperature, filtration, washing with cold water, and evaporation of the filtrate almost to dryness to expel the alcohol; the residue is treated with hot water and filtered from organic matter, and the filtrate is analyzed for phosphorus in the conventional manner. Usually two such extractions with methanol are necessary for complete extraction of the phosphorus bound to magnesium.
>
> The phosphorus bound to iron is determined in the methanol extraction residue by boiling it with 20% hydrochloric acid at constant volume for 1 hour (addition of water), followed by filtration and washing with hot water; the filtrate is evaporated to separate silicates, treated with nitric acid, and evaporated on a steam bath, the treatment is repeated, and silica is filtered off. The filtrate is analyzed for phosphorus as usual. Two or three extractions with hydrochloric acid may be necessary.
>
> Total phosphorus is done by the Eschka method. Organic phosphorus is determined on a 5-gram sample by heating with 25 ml. of 6% hydrogen peroxide to 60° until bubbles stop, evaporating to near dryness, and again evaporating with hydrogen peroxide, and the dried sample is cooled, and transferred with 0.05 *N* hydrochloric acid onto a filter until 1 liter of filtrate is collected. An additional 500-ml. extraction is done with 0.05 *N* hydrochloric acid for complete extraction and the concentrated extracts are analyzed for phosphorus conventionally. In a parallel experiment a 5-gram sample of the coal is extracted with 0.05 *N* hydrochloric acid but without the hydrogen peroxide treatment. The difference represents the organic phosphorus.

Methane. Yarovoĭ (*107*) determined the amount of methane in a coal by utilizing previously constructed isotherms of methane absorption by coal at 1 to 70 atmospheres.

> Coal samples were ground to pass a 35-mesh screen, then placed in a container and evacuated to 660 mm. of mercury, and methane was admitted to a definite pressure. This was repeated to constant pressure. The methane was then exhausted and its volume was determined. This gave the volume of methane absorbed by the coal, retained in the pores of the coal, and in the dead space of the container. The volume of methane in dead space was determined by using a nonferrous material inert to methane, of the same volume as the coal, and the volume of the methane retained in the pores of the coal was determined by using an inert porous material of same volume as the coal.

Arsenic. Bartoň and Tampa (*6*) give a method for the determination of arsenic in coal which is a modification of the methods previously described by Thorpe (*104*), Grote and Krekeler (*40*), and Boy (*10*). An approximately 1-gram sample was ignited in the Grote-Krekeler apparatus at 750° C. for 2 hours. The volatile arsenic was absorbed in 50 ml. of sulfuric acid diluted 1 to 4. The nonvolatile arsenic was determined in the ash.

Copper. Korshunov and Sazanova (*54*) determine the copper in peat ash by a polarographic method.

PLASTIC BEHAVIOR ON CARBONIZATION

Free Swelling Index. Mainz and Schwarzmann (*62*) investigated the nature of the swelling of coal during coking and the pressures exerted by it. The seat of swelling was found to be in the bright constituents of the coal, whereas the dull constituents were characterized by considerable shrinking in volume. Many samples of coal from different seams are classified on the basis of their swelling power as very dangerous, dangerous, sometimes dangerous, and harmless. The results of swelling or shrinking are similarly tabulated. One table classifies coking coals on the basis of swelling and composition. Another table gives the percentage of the different particle sizes of coal, ranging from 0 to 2 mm. to more than 10 mm., together with the percentage of moisture, volatile matter, coke, and swelling pressures exerted. Eight sets of graphs and one block-column figure show relations among coking time, rate of rise in temperature, gas evolution, and swelling properties of the charges, for several experiments.

Determination of Expansion and Carbonizing Pressure. Kushnirevich (*58*) determined the expansion pressure of coal in coking processes on batches of 10 to 11 kg. The pressure is transmitted to a lever mechanism and recorded on a scale of which 1 mm. equals 0.0016 kg. per square centimeter. The maximum pressures found with different coal sorts ranged from 0.03 (gas coals) to 0.3 kg. per square centimeter; the maximum was reached for all coals tested in 120 to 140 minutes.

Carbonization Tests. Simek and Kučera (*96*) describe an apparatus and give a method for a carbonization test.

> A charge of 100 to 150 grams of coal is placed in an aluminum liner which in turn is placed inside a steel retort and an aluminum block. This block is heated with six burners. The temperature of the coal charge is measured directly with Ni-NiCr thermocouples inserted into the coal. The distillation products in vapor form enter (1) a heavy tar condenser, (2) a light oil and water condenser with standard tape cone graduated in milliliters, (3) a hydrogen sulfide and water trap, and (4) a freezing trap. Noncondensable gases are led into a gas holder, stored, measured, and analyzed. Heavy tar condensate is heated independently to 150° ± 2° as measured with thermocouples in the block. Hydrogen sulfide is removed by passing the vapors through a city-gas cleaning mass. Residual moisture is removed with calcium chloride. For separating condensable from noncondensable material a liquid air trap is used. The noncondensable components are passed into a gas holder. The trap is gradually brought to room temperature. The crude benzene fractions remain in the trap while carbon dioxide and acetylene escape into the gas holder and are determined there. Two sets of apparatus are run simultaneously. Good agreement was obtained on per cent semicoke, heavy tar, light tar, and crude benzene; fair on total water and poor on gaseous components.

Simek *et al.* (*94*) have studied critically the known crucible coking tests and have developed a test that approaches the following conditions: The method must be suitable for any solid fuel without regard to its volatile matter; the fuel should be brought to the desired coking temperature within a short time and should be maintained at this temperature during the test; the escaping volatile matter of the primary decomposition should be superheated and the reformed carbon held back and added to the coke yield; and nonagglomerating coal should not scatter in the crucible.

> One gram of coal is weighed into a small platinum-iridium crucible, which is placed in an inverted position inside a larger crucible and covered with 10 grams of ignited silica of 0.5 to 1.0-mm. grain size. Then the larger crucible is covered with a lid (not perforated). A special electric furnace of high heat-retention capacity is brought to 1050°. Upon inserting the crucible the maximum temperature drop is 100°, and 1000° is reached again in approximately 1 minute. Total coking time is 10 minutes. Results are compared with those of other methods.

Ludmila (*61*) describes an apparatus for coal carbonization under reduced pressure.

> A lid with a conical groove is fitted to the body of a Fischer retort, which has a corresponding circular edge. To ensure tightness the retort and the lid are clamped together with a C-clamp. The heaviest distillation products are collected in a copper vessel independently heated to 100°, which serves as an electrostatic precipitator. Hydrogen sulfide is removed by a city-gas purification mass, followed by two liquid air freezing traps. The end tower contains charcoal and calcium chloride.

Dancy and De Jersey (*17*) developed an apparatus and method for a carbonization assay of coals and oil shales. Samples of about 2.5 grams are carbonized at 600°. Deviation from mean results are within ±0.3%. The results obtained with the apparatus are reproducible among themselves; there is no satisfactory correlation with other assay results. Apart from the smallness of the sample tested, other advantages are the separate weighing of the oil and water fractions, and the classification of the oils into light and heavy fractions by collection on activated charcoal and asbestos, respectively.

Gauger and Albala (*36*) have studied the petrographic characteristics and plastic and carbonizing properties of some Chilean coals.

Tejnický (*102*) used a method similar to that of Simek's crucible coking test and found that the procedure yielded quantities of coke which corresponded most closely to theoretical yields and are slightly lower than the values produced by three other methods.

Aronov and Eĭdel'man (*1*) described a method and apparatus for the determination of the yield and composition of the products of coking coal that gives reproducible results on 5- to 7-kg. batches in 3 to 3.5 hours. A furnace with temperature controls, dimensions of the chamber 300 × 150 × 400 mm., is connected in order with a tar absorber, a Cottrell-type electrofilter, a water washer, a calcium chloride drying tube, an activated carbon tube, a flowmeter, a pump, and a gas meter. The main features are total absence of losses and exclusion of air.

Richardson (*86*) carbonized in the Gray-King small scale assay apparatus as modified by Wilson and McDonald, and reports the results on the evolution of the gas and the structures of the cokes produced.

Taits and Kazakevich (*101*) have charted and tabulated their investigations showing the relationships among cokability, rank of coal, porosity, volatile matter, and carbon content.

STRENGTH OF COAL

Brown (*13*) finds that the strength of coal is not a fixed attribute but varies with previous handling of the coal. The strength of a given size of coal in a given consignment can be measured only if the sample is taken without either decreasing its strength through causing invisible breakage or increasing its strength through producing visible breakage. Sampling according to the British standard method of screen analysis is satisfactory in this respect. Shatter or tumbler tests also must not be so severe as to eliminate the effect of the previous treatment of the sample. A relatively mild shatter test giving reproducible results in duplicate samples from a given consignment was developed experimentally. Tumbler tests were also investigated. Evidence of the different strengths of coal prepared in various ways is presented.

DENSITY

Reif (*85*) discusses the true density of a porous body and defines it as the ratio of its mass to the geometric volume of a representative cube of the material.

> The experimentally determined or effective lump density of a porous body varies with the state of the body and with the inherent nature of the method used for its determination. The state of the porous body determines the value of the error made in assigning a physical boundary to a porous body. It varies with the ratio of maximum pore size to the bulk size of the material. The inherent nature of the method determines the accessibility of pore spaces to the immersion fluid. It varies with the physical properties of the immersion fluid and the particular experimental procedure. The effective lump density approximates the true lump density if the state of the body is such that its ratio of maximum pore size to bulk size is small, and if the inherent nature of the method is such that the immersion fluid does not have access to the pore space. This result is closely approximated by impregnating the coke sample with a 5% gelatin solution at 70° C.; the excess of gelatin is removed, and the sample is allowed to cool and weighed in and out of water. A routine method for determining the approximate true lump density involves drying a suitable sample (up to 30 pounds) to constant weight; the sample is then cooled and immersed in water for a definite period, drained, and weighed in and out of water. The lump density is then calculated from the weights. Coke is best evaluated from a consideration of the shatter test, bulk density, and lump density.

Franklin (*35*), in a study of the structure of carbonaceous solids by measurement of true and apparent densities, determined the true densities of a series of coals with helium and the apparent densities with methanol, water, *n*-hexane, and benzene liquids. Helium rapidly and completely fills the pore space of coals ground to pass a 72 B.S. sieve. The pore space is filled by methanol almost completely in a few hours. There is a contraction of 2.6×10^{-8} ml. for each square centimeter of surface covered by methanol. Water, *n*-hexane, and benzene almost completely fill the pore space of some low rank coals. The apparent density of such coals in these liquids is high, owing to the contraction which accompanies adsorption. *n*-Hexane and benzene penetrate only very slowly into the pore space of some coals because of the relatively large molecular diameter of these liquids. There is no appreciable volume of closed pores in coals. The pore system consists of numerous fine constrictions, and the variation in the accessibility from one coal to another is related to a variation in the width of the constrictions rather than in the mean diameter of the pores. The width of the constriction is of the same order as the diameter of simple molecule and is smallest in coals containing between 89 and 93% carbon. Porosity is assumed to be proportional to the surface area, and the latter is determined by the heat of wetting in methanol.

REACTIVITY

Jonakin *et al.* (*51*) modified the reactivity apparatus. The order of reaction with respect to oxygen was 0.81 for a Pittsburgh bed coal, 0.65 for an Indiana No. 5 bed coal, and 0.71 for a 900° experimental coke. The heating rate per unit surface varied only slightly with the sieve size of the Pittsburgh coal and coke, but varied considerably with that of the coarsely banded Indiana coal.

Roberts (*89*) describes an improved combustibility apparatus for the determination of combustion rate and ignition temperature of solid fuels and discusses the merits of producing fuels with improved combustion properties and improved appliances.

Oreshko (*74*) estimates the tendency of a coal to self-inflammation by placing 1 gram of the coal in a perforated metal cup and suspending it from a calibrated quartz spiral, heating in an electric furnace with a stream of oxygen passing through. Weight changes of sample are determined from extension of spiral while temperatures are recorded with thermocouples. Results are plotted showing weight changes, temperature of sample, and temperature of furnace for different rates of oxygen feed and temperature rise. The maximum and minimum temperature points of the weight curves do not change with variations in physical factors (rate of heating, rate of oxygen feed, size of coal) but depend only on the chemical and physical nature of the coal. Because the minimum temperature varies little for different coals, the maximum temperature can be utilized to characterize the tendency of coals to self-inflammation.

MISCELLANEOUS TESTS

Himus and Basak (*47*) find that if a sample of coal or oil shale is divided into fractions yielding percentages of ash higher and lower than that of the original material, there is a linear relationship between percentage of ash and of carbon, hydrogen, nitrogen, and sulfur. Hence, by extrapolating to zero ash, the composition of the mineral-free organic matter can be determined. The ratio of original mineral matter to ash can also be calculated. While the agreement with direct analysis is generally good, the generalization fails in some cases (carbonaceous rocks). The use of a formula of the Parr type may give wrong results.

Skinner (*98*) reviews the experimental methods of measurement of particle-size distribution and the specific surface of powdered fuels, and the advantages and disadvantages of each of them are considered. There appears to be limited application for microscopical examination and the sedimentation method was found suitable. Specific surface is not only more rapidly measured than size distribution, but appears also to give a more useful indication of fineness for the fuel engineer. The turbidity and permeability methods are both suited for rapid routine.

Duffy (*29*) gives charts for estimating total carbon, hydrogen, and oxygen from proximate analysis and by examples indicates that sufficiently exact values for most purposes can be estimated by this means without actually carrying out ultimate analyses.

Zankl (*108*) tabulates the available data for proximate analyses of Ruhr and Saar coals from 1924 to 1948.

Dean (*24*) gives proximate and ultimate analyses of 15 Ohio coals.

Review articles on various phases of analysis and testing of coal are given by Edwards (*30–32*).

Hayes (*45*) gives proximate analysis of high volatile bituminous coals of Newfoundland.

Mendoza (*67*) reviews organic and inorganic microchemical analyses as applied to gas, coal, and coke with 64 references.

Majumdar (*63*) determines colloidal graphite in oil by mixing 1 to 3 grams of sample in a mixed solvent such as benzene and alcohol plus glacial acetic acid and centrifuging at 2000 to 3000 r.p.m. After decantation the content of the tube is dried at 105° C. for 10 to 15 minutes, to determine the weight of graphite and ash. The ash is then determined by combustion.

GASEOUS FUELS

CONVENTIONAL COMPLETE ANALYSIS

Mueller (*71*) reports on method of tests used by various gas companies. Methods and studies are given for the determination of available iron in fouled purifying material, identification of materials causing pilot stoppages, protection of gas-analysis solutions, dehydration of heavy oil water-gas tars in preparation for seal formation, determination of carbon monoxide by the use of Bureau of Standards colorimeter tubes, determination of hydrogen sulfide and mercaptan, determination of water vapor adsorption of solid absorbents by the static method, determination of sediment in lubricating oil at main line stations, interpretation of corrosion tests, and determination of dew point.

Vint (*105*) in the detection and estimation of the impurities in industrial gases, determines hydrogen sulfide by iodometric titration after absorption in cadmium chloride solution and the titration of excess with thiosulfate. Nitrogen dioxide is usually absorbed in a solution of potassium permanganate containing sulfuric acid. Nitric oxide can be absorbed in ferrous sulfate or potassium permanganate solution. Phosphine can be oxidized by bromine and the phosphoric acid determined as usual. Acetylene is usually absorbed in silver bromide or fuming sulfuric acid; it can be absorbed in ammoniacal cuprous chloride solution and the moist acetylide can be filtered and dissolved in acid and the copper determined colorimetrically.

Smittenberg (*99*) gives a new method for the analysis of gaseous hydrocarbons based on high-vacuum evaporation. This method combines the advantages of two previous methods: condensation method (*14*) and measurement of the increase in vapor pressure of the condensed gas sample at gradually increasing temperatures (*93*).

> The method removes the evaporated gases continuously by means of a high-vacuum pump, and measures the amount of evaporated gases by the pressure increase in a previously evacuated chamber. The separation takes place at the lowest pressure obtainable in the apparatus. The use of more than one cooling bath has been avoided by using a metal block, cooled by liquid nitrogen, and afterward gradually increasing the temperature. The principle involved is the fact that the ratio of vapor pressures of homologous hydrocarbons increases at decreasing temperature. In approximately one hundred experiments, the results agreed within 1%. Tests were made on individual hydrocarbons, binary mixtures, and mixtures of saturated and unsaturated hydrocarbons. The advantages of the method are the small quantity of sample needed, the possibility of analyzing traces of higher components in noncondensable gases, and the relatively low cost of the analysis.

Soos (*100*) found that mercurous nitrate solution and bromine were not satisfactory for determining small quantities of ethylene, but that in mixtures of oxygen, carbon monoxide, ethylene, methane, hydrogen, and nitrogen satisfactory results were obtained by shaking the gas with a known quantity of bromine ($KBrO_3$ + KBr + acid), removing free bromine with sodium hydroxide, adding potassium iodide plus acid, and titrating the liberated iodine with thiosulfate.

Davey (*18*) in his interpretation of gas analysis shows that the characteristics of a gas which can be determined from its analysis are the heating value, the specific gravity, and the total air requirement for combustion. The Woble index (*19*) of a gas is given by $Cv/\sqrt{g}$ where Cv is the calorific value and g is its specific gravity (air = 1). An approximate straight-line relationship exists between the logarithms of the Woble indexes and those of the aeration test burner number for gases with a total inert content below 20% and heating values lying between 400 and 500 B.t.u. per cubic foot. This relation can be expressed by the equation

$$W.I. = 2.179 + 0.426 \log A.T.B.$$

Davey (*20*) has designed a nomogram for the determination of the kinematic viscosity of a gas mixture from the percentage composition. Another nomogram serves to calculate the absolute viscosity from the kinematic viscosity. A second method for the determination of the kinematic viscosity employs a triangular coordinate chart (*21*), which can be used to calculate the heating value, density, and the aeration test burner number of a ternary mixture of gases. Charts (*22*) are given for the determination of the proportions of ternary mixtures of gases which will have 500 B.t.u. per cubic foot and a specific gravity of 0.50. He (*23*) also introduces viscosity corrections into gas flow formulas.

Iavrov (*49*) illustrates the use of a graphical method for calculating the composition of generator gas produced from air-steam mixture and peat or anthracite coal.

Carbon Monoxide. Lindsley and Yoe (*59*) oxidize the carbon monoxide in air to carbon dioxide by passage over 14- to 18-mesh Hopcalite, absorb the carbon dioxide in 0.01 *N* barium hydroxide solution, and titrate the excess reagent with 0.00894 *N* oxalic acid to a phenolphthalein or thymolphthalein end point.

Oxygen. Powell and Joy (*81*) determine small amounts of oxygen in hydrocarbon gases by passing a known volume of the gas over a mat of fine copper wire which has been moistened with ammoniacal ammonium chloride solution (300 grams of ammonium chloride mixed with 1 liter of concentrated ammonium hydroxide and an equal volume of recently boiled water). The resulting blue color of the solution is measured with a photelometer at about 640 $m\mu$. The instrument is calibrated with solutions containing known amounts of copper sulfate. Mercaptans (thiols) and hydrogen sulfide must be absent.

Beckmann (*7*) uses a polarimetric method to determine oxygen in retort gas. A special cell design is shown in which 0.1 *N* potassium chloride is brought in contact with the gas stream containing the oxygen and at the same time this oxygen-saturated solution is analyzed with a polarimeter. The gas is purified before it enters the cell by means of three scrubbers containing 15% lead acetate in 15% acetic acid to remove any hydrogen sulfide and ammonia; after this a sodium carbonate scrubber is used to remove any acetic acid spray. Above a flow rate of 100 ml. per minute, the readings are independent of gas flow.

Zikeev and Shifrin (*110*) find that concentrated solutions of chromous chloride are more stable than are dilute solutions. Amalgamated zinc is preferable to zinc in reducing chromic chloride solution. A study of performance, made in a precision apparatus in which air was passed through the reagent and then through pyrogallol, showed that the fresh reagent fails to absorb about 0.14% of the oxygen present; this value increases as the reagent is used. Fresh solutions can be used for oxygen analyses which do not require high precision. The effectiveness is unaffected by temperature between 5° and 50° C.

Fogel'son and Mikhailova (*33*) confirm the use and advantages of chromous chloride for the absorption of oxygen and describe the preparation of the reagent.

Sulfur. Brady (*12*) determines the organic constituents of producer gas exclusive of mercaptans spectrophotometrically by scrubbing the gas with piperidine-ethyl alcohol solution and measuring the optical density at selected wave lengths in the ultraviolet portion of the spectrum. Thiophene is removed quantitatively by the piperidine–ethyl alcohol solution (0.5 gram of piperidine per liter of 95% ethyl alcohol) which also removes carbonyl sulfide as piperidine oxythiocarbamate and the carbon disulfide as piperidine dithiocarbamate. Extinction coefficients are determined at 230, 240, and 290 mμ. In addition, because aromatic hydrocarbons absorb at 230 and 240 mμ, a correction is obtained by scrubbing the gas with 95% ethyl alcohol and determining the extinction coefficient at 255 mμ. Equations are given for calculating the percentage of the individual constituents. The method evaluates a minimum of 0.0002 mg. of sulfur per liter.

Nussberger (*72*) determines hydrogen sulfide in digester gas by aspirating from 2 to 6 liters of the gas through 150 ml. of a 1% solution of cadmium acetate in 1% acetic acid and titrating the solution with 0.01 *N* iodine solution. The hydrogen sulfide is calculated in grains per 100 cubic feet in the usual way.

Kosior (*55*) discusses the present method of determining hydrogen sulfide in natural gas and illustrates a new apparatus.

> A sintered-glass absorption bottle is charged with 65 ml. of 1% zinc acetate and 5 ml. of 5% sodium hydroxide solutions. The gas entry valve is slowly cracked until a suitable rate of gas is flowing through the system. When the required volume of gas has passed through, the flow of gas is stopped and the meter is read again. The absorption bottle is disconnected, and added are: 12.5 ml. of diamine reagent (0.1 gram of *p*-aminodimethylaniline–hydrochloric acid in 100 ml. of 1 to 1 hydrochloric acid) and 5 ml. of 0.01 molar ferric chloride. The colors are allowed to develop for 2 hours, or 10 hours if conentration is less than 0.002 grain of hydrogen sulfide per 100 ml. of solution. After the color has developed the hydrogen sulfide concentrations are determined by comparing the methylene blue in the unknown with standard Nessler tubes or by measuring the intensity of the methylene blue colorimetric curve. Natural gas scrubbed by the Girbotol process must have diluted hydrochloric acid bubbled through it before hydrogen sulfide is determined by this method. Old sodium sulfate may contain an appreciable amount of sodium thiosulfate and thereby affect the results.

Karzhavina (*52*) reviews the methods of determining organic sulfur compounds in water gas. For large concentrations the volume method with titration of excess alkali in the absorber in which sulfur dioxide was absorbed is considered the most suitable. For traces of sulfur compounds the nephelometric method with sulfate of barium or lead is preferred.

Fogo and Popowsky (*34*) convert sulfur compounds to hydrogen sulfide in air, fuel gas, or mixtures by absorption on silica gel at about 25° followed by desorption at 500° and hydrogenation over a quartz catalyst. The hydrogen sulfide formed is preferably determined by the methylene blue method. Any hydrogen sulfide or carbonyl sulfide present in the original sample is not adsorbed by the silica gel but can be determined in the unabsorbed gas by the methylene blue and Brady methods.

Miscellaneous Determinations. Mapstone and Beckmann (*66*) determine the olefins (1) in refinery cracking cases by absorption in a solution of mercuric sulfate and sodium dichromate in 22% sulfuric acid, and (2) after removal of acid gases in a 40% sodium hydroxide solution. Ethylene (3) is determined by absorption (2) after all other olefins have been removed by absorption in 87% sulfuric acid and the resulting gas has been washed in sodium hydroxide. Higher olefins are represented by the difference between (1) and (3).

Baldwin (*5*) describes an accurate method for the determination of carbon dioxide in gas samples, which consists of drawing the gas by suction through a liquid air trap. The rate of passage is slow and is controlled by a capillary restriction connected to the vacuum pump. After all the carbon dioxide has been condensed, the trap containing it is transferred to another apparatus where the carbon dioxide is vaporized and the volume measured. A gas mixture containing 0.035% carbon dioxide can be analyzed within 20 minutes, and the result is usually accurate to within 0.003% of the original volume of the gas.

Kučera (*57*) reviews the sources of errors in the determination of gas density by means of flow rate measurements. A formula is given for the conversion of the density found by experiments on wet gas to the true density of the dry gas. A nomograph for practical usage has been developed for rapid corrections to normal temperature and pressure.

Pearson and Toye (*77*) used the Fischer reagent (a mixture of methanol, pyridine, iodine, and sulfur dioxide) which reacts specifically with water in a direct titration method for the determination of moisture in producer gas. They developed a collecting technique which overcomes condensation troubles. This method is preferred when an average value over a 10- to 15-minute period is required. The dew point method and temperature pressure method are suitable when instantaneous values are desired.

SAMPLING AND SAMPLERS

Roman (*90*) describes an automatic gas sampler which collects bubbles of gas at very regularly spaced intervals; the volume of the bubbles and the intervals at which they are collected can be regulated.

> The apparatus consists of a wide-mouthed bottle with three glass tubes passing down to the bottom of the bottle; the first tube feeds the circulating liquid (sodium chloride solution acidified with a few drops of sulfuric acid); the second tube, of considerably larger bore, is the short leg of a siphon by means of which the bottle is emptied rapidly; through the third tube the gas is sent to the gasometric flask. Finally, the gas to be sampled is fed to the bottle through a fourth tube which ends flush with the bottom of the stopper. For starting, the bottle is filled with liquid, and the siphon is started and is broken only when the level of the liquid falls to the bottom of the bottle; as the liquid is fed continuously, the level immediately begins to rise again. The breaking of the siphon opens the lower end of the tube connected to the gasometric flask, and some of the gas therefore goes to this flask, the amount depending on the rate of flow of the siphon, the rate of feed of the circulating fluid, and the difference in level between the bottom of the two tubes.

Hayman (*46*) designed a sampler for the collection of uncontaminated samples of gas from natural seepages.

> It consists of a steel cylinder of 1-cubic foot capacity, and is 18 inches long and 10 inches in diameter with 0.5-inch globe valves fitted to the slightly convex ends. These are sealed by 0.5-inch threaded steel plugs after filling. Before collection of the sample, the cylinder is filled with water. Rubber tubing is attached to a funnel, which is placed over the gas show and after the gas expels the air in the tube, it is attached to a tapered nozzle and both valves are opened. When water ceases to flow out, the valves are closed and sealed with red lead.

Reeves (*84*) collects samples of gas in proportion to main line flow by connecting an orifice on the high-pressure side of the gas line by a glass capillary, thence to a Mariotte bottle where the sample is collected. Liquid discharged from the bottle displaces gas from a second bottle back into the gas line at the low pressure side of the main orifice.

APPARATUS

Rozengart's (*92*) mercury sealing bulb closures for gas analyzers consist of two spheres: an outer one having a closed tabulation at the bottom and the usual opening to the atmosphere, and an inner one which connects to the rest of the apparatus by a stopcock and has a downward pointing capillary entering the tubulus of the outer sphere. The volume of the inner sphere is equal to the maximum size of typical samples; the volume of the outer sphere is substantially larger than that of the inner vessel. The usual mercury filling is used. These bulbs operate more smoothly than the conventional types and give less pressure differentials throughout the apparatus. The mercury meniscus in the inner bulb cannot be seen in its lowest positions, but with appropriate bulb size no leakage to the outside is possible.

Deinum and Dam (*25*) have modified an Orsat apparatus for the analysis of purified coke-oven gas, so that the ethane content of the gas can now be determined with an accuracy of 0.1 to 0.2% by volume without appreciable increase in the duration of the analysis.

Mapstone and Beckmann (*65*) have developed a laboratory gas absorber partly based on the design of Rinelli and Willson (*88*) and having a high efficiency, low back pressure, large capacity, and freedom from blockage.

Hindley (*48*) describes the Luft infrared gas analyzer.

TAR AND THE LIGHT OILS

TAR

The micro-tar meter (*80*) allows the determination of small amounts of tar in a gas; a jet of the gas impinges downward on a metal crucible and the deposit is weighed, or it impinges on a paper disk, and the blackening is determined photometrically. The latter method is used with best accuracy by comparison with a gas of known tar content and determination of the time required for equal blackening. With the former method tar contents of 30 to 10^{-2} gram per cubic meter are determined; by the latter method, 10^{-1} to 10^{-4} gram per cubic meter. The apparatus passes 200 liters of gas per hour, pressure drop 14 cm. of water.

Perna and Pelcík (*78*) estimated the naphthalene in tars by distilling 250 grams of the crude tar up to 140°.

They collect the water and light oils in a 50-ml. separatory funnel, drain off the water, dry the oil by the addition of a crystal of calcium chloride, and return it to the tar. They rectify 100 grams of the water-free tar in the Widmer column up to 215°, dissolve 0.2 gram of the distillate in 3 ml. of acetone, and pour into 150 ml. of saturated picric acid solution. After 2 hours the precipitated naphthalene picrate is filtered through a Gooch crucible fitted with a paper filter, the walls of the crucible and the precipitate are washed with 5 ml. of 0.1% picric acid, the outside of the crucibles is washed with water, and the precipitate is washed with the filter into a beaker with 100 ml. of water. The solution is boiled until all the naphthalene is volatilized (about 10 minutes), and the hot solution is titrated with 0.1 *N* sodium hydroxide. One milliliter of 0.1 *N* sodium hydroxide corresponds to 0.0128 gram of naphthalene. The results should be corrected by means of a blank titration of 100 ml. of water.

Braae (*11*) compared the xylene, acetyl chloride, and iodometric methods for the determination of water in tar. Only the iodometric method was found to give reliable results for free water. Too high results were obtained with the two other methods.

Dent *et al.* (*26*) and Raine (*82*) report on gas, destructive distillation, tar, and tar products.

Gauger *et al.* (*38*) report studies on water-gas tar.

BENZENE, TOLUENE, XYLENE

Gepnerowna-Szpakowska (*39*) made determinations of benzene, toluene, and other fractions in tar and similar products and in the intermediate products of tar distillation. A description of Colman and Yeoman's method (*15*) is given. The same fractions were also distilled by the Spiker and Benzol-Verein methods (*79*) and comparisons in composition were made.

Doliński and Boguńska (*27*) describe a laboratory fractionating apparatus and procedure. The fractions of benzene, toluene, and xylene obtained from a commercial product were in close agreement with those distilled from a prepared mixture of the three ingredients.

Mirel *et al.* (*69*) have developed a method for determining small amounts of benzene in ethyl ether. By making use of the difference in specific gravity of benzene (0.879) and ether (0.720), the benzene content can be determined within 0.05% of the volume of the sample.

Kouba *et al.* (*56*) have developed two methods for the determination of benzene in ethyl alcohol that are accurate to within 0.02% of the volume of the sample. One depends on the difference between the refractive indexes, the other on difference between their specific gravities. Small amounts of ether do not interfere. Ether and ethyl alcohol are separated by distillation and extraction with saturated sodium chloride solution.

Löfgren (*60*) gives a method for the separation of *m*-xylene from crude xylene.

The method is based on selective sulfonation of *m*-xylene followed by selective hydrolysis of *m*-xylene sulfuric acid. Crude xylene (500 grams) is shaken mechanically 2.5 hours with 475 grams of sulfuric acid, added in three steps, the mixture is stirred and refluxed 1 hour at 70° to 80° and cooled, 125 ml. water are added, and the *p*-xylene layer is separated (yield 190 to 210 grams). The solution of sulfuric and sulfonic acids is refluxed 3 hours at 127° to 130°, adding water as needed to keep the temperature down; when cool, more water is added and the *m*-xylene is separated, washed, dried, and distilled (yield 206 to 220 grams; 75 to 80%). The product compares favorably with that of highly purified *m*-xylene.

Wilson (*106*) determines traces of organic bases in benzene by titration with 0.02 *N* perchloric acid in glacial acetic acid under anhydrous conditions, with methyl violet indicator. To 50 to 500 ml. of benzene 10 to 25 ml. of glacial acetic acid and 2 ml. of indicator solution (0.01 gram of methyl violet in 100 ml. of glacial acetic acid) are added, and the solution is titrated to a blue-green end point with 0.02 *N* perchloric acid.

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FERROUS METALLURGY

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PRACTICAL advances in ferrous analytical chemistry result from a correlation of available information with experience in selecting the most likely approach to solution of a specific problem. Frequently these advances are made under the compulsion of need for new or better data on experimental operations or new experimental alloys, and the chemist utilizes the store of basic information in the literature along with new reagents and tools as a basis for devising the method best suited to his requirements and the working facilities at his disposal.

BASIC INFORMATION

The papers of Furman, Mason, and Pekola (*24*) and of Sandell and Cummings (*76*) on extraction of metal cupferrates and of Hunter and Wells (*45*) on separation of iron in metallurgical analysis will be welcome references for analytical chemists, as will those of Burstall and co-workers (*9*), who utilized chromatographic methods for separation of metals, and Irving, Risdon, and Andrew (*49*) dealing with improved methods for determining traces of metals. Hoste (*44*) described a new specific reagent for copper (2,2-diquinolyl) which forms a complex that can be extracted from aqueous solution with organic reagents.

The reaction mechanisms of two common analytical procedures, oxidation of divalent manganese to permanganate and reduction of ferric iron with sulfurous acid, were investigated by Strickland and Spicer (*82*) and Burriel-Marti and Conde (*8*), respectively. Irving and associates (*48*) and Davenport (*18*) investigated some of the reactions of 8-hydroxyquinoline derivatives that are of interest to metallurgical analytical chemists. Jewsbury and Osborn (*51*) investigated the use of morin for the colorimetric determination of boron. The use of zirconium oxychloride (*84*), titanium hydroxide (*66*), and zirconyl chloride or nitrate (*42*) has been investigated for the separation and determination of phosphorus.

Lingane (*58*) described some of the more recent developments in electroanalysis. Connick and McVey (*15*) investigated the reactions of zirconium in aqueous solution.

Methods for the separation of calcium from magnesium were investigated (*30, 43, 47*).

Nutten (*65*) recommended ferrous propylenediamine sulfate as an oxidimetric standard.

Chapman, Marvin, and Tyree (*10*) determined the degree of volatilization of 39 elements from mixtures, of hydrofluoric and perchloric acids. Boron, silicon, germanium, arsenic, antimony, chromium, selenium, manganese, and rhenium were found to be lost to varying degrees.

A direct x-ray method for the analysis of stainless steels was described by Cordovi (*17*), while Euw (*22*) analyzed slags by means of their x-ray spectra. Eeckhout (*20*) analyzed stainless steels quantitatively with the spectrograph for chromium, nickel, molybdenum, titanium, copper, and columbium by using an acid solution technique. Weaver and Brattain (*90*) described a semiquantitative spectroscopic method using lithium carbonate as a flux, that was said to be applicable to any inorganic material. Feldman (*23*) used spark excitation and a porous cup electrode for the direct analysis of solutions. Klinger and Schliessmann (*55*) described a method for analyzing very small surface areas by sparking through a mica diaphragm with a 10-micron opening using a 1-mm. diameter silver or copper electrode and a conventional spectrograph.

A book (*12*) devoted to a description of methods of analysis used and found to be most reliable in the laboratories of the publisher is a useful, practical reference.

SPECIFIC METHODS

Aluminum. Aluminum is being utilized to an increasing extent in the manufacture of steels for deep drawing applications. A study of methods for preparation and use of aluminon for the colorimetric determination of this element was made during the past year (*80*). Chenery (*13*) found thioglycolic acid useful in inhibiting the reaction of iron when determining aluminum colorimetrically with aluminon. Thrun (*88*) described a procedure for the synthesis and use of eriochromcyanine for the colorimetric determination of aluminum in an iron-free solution. Wiberly and Bassett (*91*) reacted aluminum with 8-hydroxyquinoline after removing the iron from solution with the mercury cathode. They then extracted the quinolate with chloroform and measured the transmission of the extract at 390 mμ to determine aluminum spectrophotometrically. Osborn and Jewsbury (*70*) explored the conditions necessary for separation of beryllium from aluminum using ammonium benzoate. Methods for determining the amount of aluminum in steel as the oxide (*14*) and as the nitride (*5*) were described. The steel is dissolved away from the alumina with hydrochloric acid, the residue is fused and the melt is taken up in acid, iron is added as an internal standard, and the solution is excited with a high voltage condensed spark as it drops into the spark gap; the aluminum is determined by conventional spectroscopic methods. Aluminum nitride is separated by dissolving the steel with an ester-halogen solution and its nitrogen content is determined in the usual way.

Carbon. Carbon was determined spectroscopically in steel during the past year (*69, 85, 86*). The carbon line at 2296.8 A. and the iron line at 2311.3 A. were used and both the alternating current arc and the condensed spark were investigated as means of excitation. These methods apparently are not yet in widespread use. Harrison (*34*) explored the conditions necessary for the determination of combined carbon in cast iron by measurement of the absorption of the brownish-yellow color formed when the iron is dissolved in nitric acid of specific gravity 1.20.

Cerium. Cerium was determined (*60*) by potentiometric titration with Mohr's salt after removal of iron with the mercury cathode, oxidation of the remaining chromium and manganese with ammonium persulfate in the presence of silver, and precipitation of the titanium and cerium with ammonium hydroxide.

Copper. Copper was determined spectrophotometrically by Mehlig and Durst (*64*) by measuring the transmission at 650 mμ of the blue color formed upon adding an excess of triethanolamine to the acid solution containing copper. Steele and Russell (*81*) utilized the gum acacia–stabilized complex of copper with diethyl dithiocarbamate in ammoniacal solution for the same purpose.

Chromium. Potassium bromate was used by Harrison and Storr (*36*) to oxidize chromium selectively without oxidizing manganese to permanganic acid. The oxidized chromium was then determined by conventional procedures. The method was found to be applicable to such materials as ferrochrome, stainless steels, and irons.

Columbium. Geld and Carroll (*25*) presented a method for determining relatively small amounts of columbium and tungsten in high-temperature steel alloys. They utilized the yellow percolumbic acid formed by action of hydrogen peroxide upon solutions of columbium in concentrated sulfuric acid and tungsten thiocyanate formed by reduction of tungsten with stannous chloride as a basis for their color measurements. Waterkamp (*89*) reviewed properties of columbium and tantalum salts of interest in analytical chemistry.

Germanium. Germanium in oxalate form was separated from such elements as vanadium, ferric iron, zirconium, thorium, and aluminum with tannin by Holness (*40*). Germanium was found to precipitate at a lower acidity than was required for tin and tantalum and at a higher acidity than was needed for titanium.

Manganese. Nydahl (*67*) investigated the use of ammonium persulfate for oxidation of manganese in the colorimetric procedure in place of periodate. He stated that it was superior, under proper conditions of use, especially for extremely small amounts of manganese.

Molybdenum. Potassium iodide (*28*) was added, to acid solution, in place of stannous chloride as a reducing agent in the determination of molybdenum by the thiocyanate method. The intensity of the colored thiocyanate in aqueous solution was measured without extraction. Zinc amalgam (*95*) was used as a reducing agent in the determination of relatively large amounts of molybdenum and titanium. The reduced molybdenum was titrated with standard potassium permanganate. The titanium was titrated with ferric chloride in the presence of thiocyanate.

Nickel. Adelt and Gruendler (*1*) described a procedure for determining nickel colorimetrically with dimethylglyoxime in a strongly ammoniacal solution. Procedures for determining phosphorus by the molybdenum blue method, chromium as the diphenylcarbizide, and molybdenum as the thiocyanate were also given. A polarographic procedure for determining nickel and copper was described by Stromberg and co-workers (*83*). Ikenberry and Canfield (*46*) described a rapid method for determining nickel on the surface of steel sheets.

Nitrogen. Mercuric chloride was used in an oxygen-free atmosphere by Baxter (*4*) to liberate nitrogen and oxygen from irons and steels. These gases were recovered quantitatively. By use of larger than usual amounts of potassium sulfate during digestion, Epelbaum and Ormont (*21*) reduced the time necessary to decompose the acid-insoluble nitrogen compounds in alloy steels to from 6 to 8 hours. Hague, Paulson, and Bright (*32*) demonstrated that under suitable conditions hydrogen peroxide was effective in decomposing these compounds, so that an accurate value for total nitrogen could be obtained on steels containing such "acid-insoluble" nitrogen compounds as titanium nitride.

Kempf and Abresch (*52*) found that certain grades of ferromanganese (16 to 44% manganese) contain nitrogen compounds not converted to ammonium chloride on treatment of the sample with hydrochloric acid. A relationship between the silicon content and this unconverted nitrogen was said to exist and dilute sulfuric acid was found effective as a substitute for hydrochloric acid. Hydrochloric acid was said to be satisfactory for pig irons, spiegel, open-hearth steel, and ferromanganese containing 70 to 90% manganese. Maltsev and co-workers (*61*) showed that nitrogen could be determined by direct nesslerization of the neutralized electrolyte following removal of iron with the mercury cathode. Machemer and McNabb (*59*) reported results of some experiments made to determine the precision and accuracy of the steam distillation semimicromethod for distillation of 15- to 40-mg. quantities of ammonia.

Nonmetallic Compounds. The importance of the manner in which different elements are combined in steels is gaining increased recognition. Most of the published work over the past year on methods for isolating compounds from steel for study has described procedures for the separation, analysis, and identification of carbides (*6, 11, 29, 37, 39, 54–57, 62, 63, 72–75, 77, 78, 94*). Most of these involved electrolysis with an aqueous electrolyte.

Hydrochloric acid (1 to 10) was used for high-speed steels (*6*). An electrolyte of 6% ferrous sulfate with 0.2% sodium citrate and 7% sodium chloride was used at a current density of 0.5 A. per sq. cm. (*11*). Aqueous bromine was utilized by Heczko (*37*) as a solvent for the steel matrix. Hofmann and Deponte (*39*) used 3% hydrochloric acid as an electrolyte. Klinger and Koch (*54*) used as anolyte a 10% solution of sodium citrate containing potassium bromide and iodide and a catholyte of cuprous bromide. The isolated residues were separated into various fractions by treatment with anhydrous chlorine at temperatures in the range of 200° to 250° C. and the resulting chlorides were removed by sublimation in vacuum.

Koch (*56*) separated carbides by electrolysis in acid. Maurer used aqueous sulfuric acid (300 ml. per liter) for separating columbium carbide (*62*) from stainless steel and 9% hydrochloric acid for isolating titanium carbide (*63*). Popova and Platonova (*74*) separated iron and chromium carbides from austenitic steels by electrolysis at a current density of 0.02 A. per 100 sq. cm. in an electrolyte made 1 *N* in potassium chloride and 0.2 *N* in hydrochloric acid and containing 0.5% sodium thiosulfate. Popova and Rybina (*75*) used an electrolyte of 1 *N* potassium chloride containing citric acid. Wranglen (*94*) expressed the opinion that many of the electrolytic methods for extracting nonmetallic compounds from steel were not valid from a theoretical standpoint. Goldschmidt (*29*) compiled useful x-ray data on many of the carbides likely to occur in steel.

Jack (*50*) verified x-ray data on the iron-carbon, iron-nitrogen, and iron-carbon-nitrogen systems and developed useful new data. Beeghly (*5*) described a method for separating aluminum nitride from steel by use of ester solutions of bromine or iodine and supplied data on the behavior of this compound in steel during thermal treatment. Kitahari (*53*) found a neutral solution of ferric chloride to be a useful reagent for separating iron from silicides, sulfides, etc., in sponge iron.

Phosphorus. Harrison (*35*) made a study of the molybdenum blue method for determining phosphorus in hematite iron and steel. He concluded that the method may be used in a composite plan of analysis, and that it is more sensitive but the color is less stable than the phosphovanadomolybdate color complex.

Selenium. Selenium was recovered in the insoluble residue from solution of the steel in 1 to 4 sulfuric acid and weighed by a procedure described by Tananaev and Murasheva (*87*). The method was said to be as accurate as A.S.T.M. method E 30–45 and much simpler.

Silicon. The reaction of silicon in the form of silicomolybdic acid with such bases as hexamethylenetetramine, pyridine, and 8-hydroxyquinoline was made the basis for both gravimetric and volumetric methods of determining small amounts of silicon by Duval (*19*). The influence of other elements on the applicability of the method was not reported. Wilson (*92*) investigated this method and found that silicon as the quinoline silicomolybdate could be precipitated quantitatively from a strong hydrochloric acid solution, filtered off, and dissolved in standard sodium hydroxide, and the excess titrated with standard acid. This volumetric method was found to be rapid, accurate, and applicable to such materials as refractories and silicon irons. Hill (*38*) described a colorimetric procedure for determining silicon in low-alloy and carbon steels by use of the silicomolybdate complex.

Sulfur. Geuer (*26*) determined sulfur nephelometrically as lead sulfite after absorbing the products of combustion of the steel sample in oxygen with lead acetate. Pepkowitz (*71*) described a method for determining microgram quantities of sulfide sulfur by oxidizing the hydrogen sulfide liberated by hydrochloric acid from the sample with an excess of calcium hypochlorite; the excess hypochlorite is then titrated with iodine. The method is empirical.

Tin. A polarographic method for determining tin in steel after separating it as stannic chloride was described by Allsopp and Damerell (*2*). In a method for determining the tin content of high-speed steels used by Bagshawe and Dyke (*3*), the tungsten is separated as the carbide in hydrochloric acid solution, and tin is removed as the sulfide, subsequently reduced to the divalent state with metallic aluminum in the presence of antimony, and titrated with standard iodate.

Titanium. The colored complex of titanium with hydrogen peroxide was utilized (*27, 31*) for determining titanium in alloy steels without removal of such elements as chromium and nickel.

Shippy (*79*) reduced iron and titanium in the Jones reductor and titrated the reduced solutions with standard potassium permanganate. Methylene blue was used as the indicator for titanium and *o*-phenanthroline for the iron end point.

Tungsten. Budanova and Gavrilova (*7*) separated columbium and tungsten with cupferron in the presence of fluorides and then determined tungsten as the thiocyanate in a reduced solution. Wood (*93*) also described a procedure for determining tungsten as the thiocyanate after reduction with stannous chloride.

Vanadium. Cooper and Winter (*16*) made a thorough investigation of the variables in the determination of small amounts of vanadium in low-alloy steels and described a method for the precise colorimetric determination of these amounts by converting them to the phosphotungstovanadate complex. Gillod (*27*) described a method for the simultaneous determination of this element and titanium in the form of their complexes with hydrogen peroxide by measurement of their transmission at 520 and 460 mμ, respectively.

Zirconium. The use of tannin in the determination of zirconium was investigated by Holness and Kear (*41*), who found that zirconium and titanium could be precipitated in acid solution with tannin while the iron and aluminum remained in solution. They found tannin superior to cupferron and called attention to an error which may result if silica is introduced into the analysis as an impurity in such reagents as ammonium hydroxide. Hahn (*33*) found mandelic acid to be suitable for determining small quantities of zirconium. Oesper and Klingenberg (*68*) synthesized and studied a number of derivatives of glycolic acid to determine their specificity and value as quantitative precipitants for zirconium. *p*-Chloromandelic and *p*-bromomandelic acid were found to be most promising.

SUMMARY

In this review of developments in ferrous analytical chemistry over the past year the literature references cited do not include all published articles; an endeavor was made to include those of specific value to laboratories analyzing a variety of ferrous materials. It is hoped that any important 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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THE review in February 1949 (*16*) outlined the present status of analytical chemistry in the field of nonferrous metallurgy and particularly emphasized the trend toward the development and use of instrumental techniques. This review, while mainly concerned with developments and work during the past year, of necessity also touches upon data which actually appeared during the previous period but were not available when the first review was prepared.

The trend toward instrumentation and special techniques in analysis continued in the field of nonferrous metallurgy. Typical procedures involving specialized instrumentation are covered in the following references. Apparatus of an automatic nature for the electrochemical analysis of nonferrous metals was described by Kovalenko (*56*), and Duval covered the subject of automatic gravimetry (*24*).

Adsorption and absorption techniques, hitherto of little import in the nonferrous field, were discussed in seven papers (*46, 52, 55, 59–61, 109*). Although such procedures involving chromatography and similar methods are not in general use, their utility in specific applications should not be overlooked.

Hillier (*44*) points out the possibilities involved in the use of the electron microscope as a tool for microanalysis. Such procedures have certain possible applications in the nonferrous field. In the somewhat related field of x-rays, papers by Alexander and Klug (*2*), Geisler and Hill (*30*), and Duwez and Odell (*25*) indicate that the nonferrous analytical chemist has a new technique available which may solve certain specific problems.

POLAROGRAPHIC AND AMPEROMETRIC PROCEDURES

The growing importance of polarographic and amperometric procedures in the nonferrous field is attested by the fact that during the year upwards of 75 papers on such procedures specifically pertinent to nonferrous analytical chemistry have appeared. Only a few references are here cited as typical of the growing interest in this field of analysis. Kolthoff has discussed amperometric titrations (*53*). Heyrovský has given an optimistic but interesting discussion of modern trends of polarographic analysis (*43*). Stross has published a most interesting and valuable survey article on the polarographic analysis of light metals and alloys (*103*). Moritz's paper on the theory and development of polarographic equipment and methods in industrial laboratories (*75*) is a stimulating bit of work and well worth the attention of those interested in the possibilities in this field. Kolthoff's article on voltammetry and amperometric titrations (*54*) in *Frontiers in Chemistry* should be a "must" on the reading list of all nonferrous analytical chemists, as should be Lingane's polarographic theory, instrumentation, and methodology (*64*). References to the many articles on specific applications of polarographic or amperometric procedures to particular problems have been omitted, for such references are readily available in *Chemical Abstracts* and elsewhere.

Two papers by Lingane on electroanalytical methods are well worth the attention of those interested in such procedures and their possibilities: controlled electroanalysis (*65*) and some new developments in electroanalytical chemistry (*66*).

An ever-present problem in nonferrous analytical laboratories is that of distinguishing common metal alloys by means of spot tests or similar procedures. Bennett has presented an interesting paper on distinguishing the common metal alloys (*10*), while Winslow and Liebhafsky have looked into the spectrophotometric aspects of spot testing (*110*). Other papers on the identification of alloys of various types are available. Goldberg covers zinc die casting alloys (*35*), and Witcoff and Simpson touch on aluminum alloys (*111*), as do Niessner (*77*) and Kuznetsov (*57, 58*). The latter author also presents valuable hints for increasing the sharpness of color tests.

SPECTROCHEMICAL ANALYSIS

There has been a veritable flood of publications concerning nonferrous analysis by means of spectrographic procedures. Although "Practical Spectroscopy," by Harrison, Lord, and Loofbourow (*38*), is the most recent comprehensive text on spectrochemical analysis, the texts cited in last year's review are still pertinent; no startling new developments have occurred. However, specific mention is made of the volume entitled "Modern Instrumental Analysis" (*11*). This text is a compilation of review articles by authorities in various fields of instrumentation. The chapters on spectrochemical analysis by J. R. Churchill are of special interest to nonferrous chemists and are illuminating, instructive, and comprehensive.

Although a number of references are cited to published work on spectrochemical analysis pertinent to the field of nonferrous metallurgy, such papers are not discussed in this review, other than to say that in the reviewer's opinion they do not represent any particularly novel approaches to the problem of analysis, but rather refinements in existent procedures or the application of specific practices to specific materials and problems. The titles are many and varied and the interested reader can doubtless select those of particular interest to him (*1, 3–9, 12–15, 17–23, 26–29, 31–34, 36, 37, 39–42, 45, 47–51, 62, 63, 67–74, 76–102, 104–108*). The status of spectrochemical analysis in the nonferrous field has not changed materially during the year, though possibly in the references cited there are seeds of progress, the fruition of which will be greater and better use of such procedures.

There has been steady progress in the field of direct-reading spectrographic instruments and procedures. In one industrial metallurgical concern, 28% of the reported determinations, about 1,120,000 out of 4,000,000, were made on direct-reading spectrographic instruments. Two types of instrumentation are commercially available at the present time—that of Baird Associates of Cambridge, Mass., and that of Applied Research Laboratories of Glendale, Calif. Other instrument houses are doing work in this field and additional sources of instrumentation may be shortly available.

Mention should be made of the trend toward the wider use of flame photometry in the nonferrous field. Acceptable instrumentation of two types is currently commercially available. The Perkin-Elmer Corporation markets an instrument of the filter type which is of considerable interest. This instrumentation has been more generally acceptable since the incorporation of the necessary elements which made possible the use of internal standard methods. The other type is that popularly called the Beckman instrument, produced by National Technical Laboratories. This instrument is of the monochromator type and has been successfully applied in various phases of the nonferrous field, particularly where the rapid and accurate determination of the alkali metal elements and calcium is of essential importance.

There is a growing use of colorimetric or photometric methods in the nonferrous field. This growing interest has been greatly stimulated by the progressive activity of Committee E-3 on Chemical Analysis of the American Society for Testing Materials.

The expanding use of statistical methods for the evaluation of the adequacy of particular methods as regards accuracy and precision is worthy of notice. Quality control statistical methods ordinarily used to control quality of products, both step and final, are being more and more widely used to evaluate the analytical work of routine analysts in many industrial analytical laboratories.

In general, chemical analysis in the nonferrous field is in a healthy, dynamic state of growth and development. The author of this review feels that this condition is reflected by the contributions that have been made during the recent past to the literature pertinent to the nonferrous field, which includes not only items of general interest but also items concerned with the determination of specific elements or groups.

INSTRUMENTAL METHODS

It may seem that this review unduly stresses the importance of instrumental methods of analysis. The author feels that the emphasis given is but an accurate mirroring of what actually is occurring in the field, but he also has a word of caution. Many of these instrumentalized techniques are essentially repetitive in nature. The validity and integrity of the results obtained depend fundamentally upon the standards by the use of which the instrumental techniques are set up, calibrated, adjusted, and maintained. These standards must be calibrated and evaluated by the more laborious and time-consuming classic or traditional methods, which are satisfactory in general from the standpoints of accuracy and precision of results, but are woefully lacking in speed. Speed and ease of application are major advantages of most of the newer repetitive instrumentalized procedures and speed in obtaining reliable and trustworthy analytical data is essential to modern nonferrous metallurgical practice. Curiously enough then, refinement and improvement of the traditional methods become more and more important as their actual use in routine metallurgical laboratories diminishes. More dependable and reliable assignment of values to standards for use in instrumental analysis makes the quality of results obtained by traditional methods of paramount importance. A remarkable and somewhat paradoxical trend in nonferrous metallurgical analytical chemistry is that fewer traditional analytical chemists are required but their importance is growing. The trend in modern nonferrous analytical laboratories is for more workers who can be trained to push buttons, throw switches, and read dials, and fewer but better real analytical chemists.

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PETROLEUM

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THE present review of progress in analysis in the field of petroleum takes into consideration the literature for approximately one year from that covered in the previous review (*78*). As may have been expected, there has been an abundance of publications, doubtlessly still reflecting accumulated intellectual production of the war years.

CRUDE OIL

Dickey and Sorg (*23*) described an electrometric titration procedure for determining inorganic chlorides directly in crude oil, avoiding the customary preliminary water extraction, and thus permitting a determination to be completed in 20 minutes.

GAS

Parker and Goldblatt (*101*) identified isobutylene by absorption in phenols with catalyzed formation of 4-*tert*-butylphenol whose melting point he determined, and Kivensen *et al.* (*68*) described an infrared chopped radiation analyzer for the determination of butadiene in recycle streams of synthetic rubber plants. The instrument can be adapted for recording and control purposes. Jezl and Hablitzel (*58*), working on butadiene, described a simple distillation apparatus for separating dimers from monomers; the column is adaptable presumably to other separations in which small amounts of relatively high boiling materials must be removed from volatile samples. Milsom *et al.* (*94*) combined infrared and mass spectrometry for analysis of gaseous mixtures, because infrared is more reliable for isomers whereas mass spectrometry is more efficient when isomeric distribution is not required. In the calculations the infrared calibration coefficients and mass spectrometer sensitivities are placed in the same reciprocal matrix.

Mapstone and Beckmann (*89*) reviewed methods for determining total unsaturation and applied a reagent comprising mercuric sulfate and sodium dichromate in sulfuric acid to refinery cracking gases. Webber (*132*) employed a carbon dioxide stripping and scrubbing procedure to determine butane in furfural when evaluating stripper efficiency. It was also applied to mineral seal oil recovered in oil absorption processes. Robey and Wiese (*109*) described a scheme of complete analysis for mixtures of C_5 hydrocarbons involving high efficiency distillation and dilution of the fractions with a gas to permit the application of established methods of gas analysis. Included is a new colorimetric method for isoprene involving mercuric acetate reagent.

Starr and Lane (*117*) studied the results of a great many tests from many laboratories employing instrumental, ordinary physical, and chemical procedures for the determination of gaseous hydrocarbons in the Rubber Reserve butadiene program and drew conclusions on the unique advantages of each of the procedures. Smittenberg (*114*) described a micromethod (0.5-ml. sample) for analyzing hydrocarbon gases based on low pressure evaporation and measurement of pressure increase in an evacuated receiver. Crouthamel and Diehl (*21*) analyzed binary mixtures such as air with methane, carbon dioxide, or hydrogen by measuring the velocity of sound in the mixture; the signal was amplified electronically and registered on a meter that can be calibrated in terms of the composition of the gas mixture to give a continuous reading of composition of the gas flowing through a tube. The apparatus is distinguished in basic principles from that of the General Electric Company. Lewis (*80*) described an improved Blacet-Leighton apparatus for microanalysis of gas.

Brooks *et al.* (*11*) described methods and apparatus for the analysis of fixed and hydrocarbon gas mixtures frequently encountered in the petroleum industry. The apparatus is comprised of unit sections permitting versatile applications and embodies mechanical mercury lifts. Specially prepared copper oxide is used in the determination of paraffins by combustion at 700° C. without addition of air or oxygen. Orchin and Wender (*100*) described apparatus claimed to be specially useful for reactions in which it is necessary to measure gas absorbed or evolved, such as hydrogenation, dehydrogenation, etc. Sobcov and Hochgesang (*116*) applied an infrared gas analyzer to the continuous determination of carbon monoxide and carbon dioxide in the flue gases from catalytic cracking operations. Included is a description of principle and procedure for operating the instrument.

Brady (*8*) described a method for determining trace quantities of oxygen in fixed gases based on the fact that a solution of sodium anthraquinone-β-sulfonate is colorless when oxidized but red when reduced. In the latter state it reacts quantitatively with oxygen, and photoelectric measurement of the color change forms the basis of the determination. Deinum and Dam (*22*) modified the apparatus of Uhrig for determining small quantities of oxygen in gaseous mixtures. Beckmann (*5*) described a polarographic method for determining oxygen in retort gas. Powell and Joy (*104*) described a portable apparatus for determining low concentrations of oxygen, involving photoelectric intensity measurement of the blue copper-ammonia complex resulting from oxidation of copper wire and solution of the oxide in ammoniacal ammonium chloride solution.

Cherry (*14*) determined water vapor in gases by thermal conductivity, continuously and recording. Gallaway (*36*) determined water in gaseous propane by infrared absorption from 5.8 to 6.3 microns, claiming an accuracy of 0.1 mg. of water per liter of gas. Riesenfeld and Frazier (*107*), concerned with processes for dehydrating natural gas, considered dew point, infrared absorption, conductivity, and various chemical methods and concluded they were not reliable for effluent gases from processes employing hygroscopic organic liquids such as glycol or glycolamine mixtures and adopted one in which the individual constituents of the vapor are determined; water is calculated by difference. Hasegawa and Simard (*46*) employed an automatic recording infrared absorption gas analyzer for the continuous determination of components in the product gas stream from an ethylene oxide pilot plant and discussed advantages of this type of analytical control.

GASOLINE

Anderson and Seyfried (*3*) studied the relationship between molecular structure of organic compounds and their infrared absorption spectra, and discussed the general principles of the method and the various oxygenated functional groups and olefins that can be determined in hydrocarbon synthesis naphtha. Hibbard and Cleaves (*48*), working in the near infrared with a small glass prism spectrometer, determined the average number of CH_3, CH_2, and aromatic CH groups in hydrocarbons, as well as the amount of chain branching in paraffins and degree of substitution on naphthene and aromatic rings. Johnston *et al.* (*59*) combined silica gel adsorption with infrared analysis to differentiate unsaturation in catalytically and thermally cracked gasolines.

Raman spectrometry was applied by Heigl *et al.* (*47*) for the determination of total olefins and total aromatics employing functions of the areas under the recorded peaks rather than peak heights because the positions of the peaks shift slightly with different compounds. Rampton (*105*) described a procedure involving silica gel adsorption and selective hydrogenation for determining types of hydrocarbons in cracked gasoline, the classes being aromatic, naphthenes, paraffins, noncyclic olefins, and cyclic olefins. Thomson (*123*), in a modification of Kurtz's method based on refractivity intercept, presented a nomograph for calculating paraffin and naphthene ratio in gasoline freed of aromatics and olefins.

Marquardt and Luce (*91*) employed mercuric acetate to determine unsaturated compounds such as styrene and its derivatives, completing the determination with an ammonium sulfocyanate titration of mercury equivalent to the unsaturated compound. Martin (*92*) determined styrene and certain homologs by titrating the acetic acid liberated when the unsaturated compounds react with mercuric acetate in methanol solution. Glasgow *et al.* (*39*) analyzed recycle styrene for its major component by a combination of distillation, azeotropic distillation, and freezing point. Anderson and Zerwekh (*4*) described an infrared procedure for the determination of individual impurities in *n*-heptane concentrates of greater than 99.0% purity. Seven impurities were determined with an average accuracy for individual impurities of ±0.2% of the total sample.

Kouba *et al.* (*71*) determined small quantities of benzene in ethyl alcohol by adding water, distilling, and applying refractive index or density to the hexane extract of the azeotrope, claiming an accuracy of 0.02% on basis of the sample. Kaye and Otis (*61*) determined isomeric xylene and ethylbenzene in carbon disulfide by infrared analysis. Tunnicliff *et al.* (*126*) described an ultraviolet absorption procedure for the determination of C_6, C_7, and C_8 aromatic hydrocarbons in a mixture, based on absorption measurements at a number of wave lengths. Interfering unsaturates or sulfur compounds are eliminated by prior aqueous mercuric nitrate treatment and correction is applied for loss of benzene to the aqueous solution. In another paper Tunnicliff *et al.* (*127*) presented an algebraic method to correct for interfering absorption in spectrophotometric data.

Conrad (*18*) described a rapid silica gel adsorption method for the determination of aromatic hydrocarbons in petroleum products, involving addition of a hydrocarbon-soluble fluorescent dye to the sample and subsequent ultraviolet illumination of the column to permit measurement of the fluorescent band which is a measure of aromatic content. O'Connor (*99*) employed an added dye in a silica gel adsorption procedure to determine hydrocarbons and oxygenated materials in a study of products from hydrocarbon synthesis. Morris *et al.* (*96*) described a simple procedure for determining one or two small impurities in aromatic hydrocarbons, based on the influence of impurities on the true boiling point of the major components where the boiling points of the impurities are considerably removed from that of the main constituent. Accuracies of 0.01 to 0.10% are claimed.

In gasoline containing over 40 p.p.m., Mapstone (*87*) detected diphenylamine by the blue reaction product, in the aqueous layer, when the sample is shaken with 1 ml. of concentrated hydrochloric acid and a crystal of sodium nitrite. Though not as sensitive as the ammonium vanadate procedure, it is more reliable. By determining optical density at 290 millimicrons on the alkaline extract of gasoline, Murray (*98*) determined phenols in gasoline and in cresylic acids. Interferences are discussed and the importance of a minimum concentration of 0.4% sodium hydroxide, to avoid hydrolysis of phenolates, is emphasized. Thomas *et al.* (*121*) described a colorimetric method for determining inhibitor, such as alkyl-substituted aminophenols and *p*-phenylenediamine compounds, in gasoline. The method involves extraction of the inhibitor with dilute hydrochloric acid, adjustment of pH to 5.8, and addition of hydrogen peroxide to develop a pink color. Mapstone and Beckmann (*88*) described a number of color tests for detecting phenols in gasoline. Traces of organic bases in benzene were determined by Wilson (*134*) by titration with perchloric acid in glacial acetic acid to methyl violet indicator. Kubis (*74*) determined tetraethyllead in gasoline by brominating and determining lead in the aqueous layer polarographically. Kroller (*73*) determined tetraethyllead in gasoline by precipitation with iodine monochloride and perchlorate titration of the precipitate.

KEROSENE AND HEAVIER FUELS

Coggeshall and Glessner (*16*) described an ultraviolet absorption method of analyzing hydrocarbon mixtures boiling in the kerosene range, for naphthalene and methylnaphthalenes, based on data taken at three wave lengths on cuts made between specified temperature limits and correcting for background absorption due to other unsaturated compounds. Anderson (*2*) also described an ultraviolet absorption method for individual naphthalenes and for total naphthalenes, the latter based on absorption measurements at two wave lengths.

LUBRICATING OIL

Freymann and Freymann (*35*) applied infrared absorption to analyze lubricants comprising fatty oils, mineral oils, and shale oil, and Fred and Putscher (*34*) found that the characteristic absorption at 10.3 microns serves to identify oils, etc., derived from Pennsylvania Grade crudes, and presented evidence that this characteristic absorption is due to olefins. Hooper (*52*) described a procedure for determining dissolved oxygen in liquid petroleum products and furfural, involving removal of dissolved gas by agitation under reduced pressure in a special degassing vessel and analysis of this gas for oxygen in conventional manner. Golden (*41*) described a method for detecting and determining peroxides in heated mineral oil and petrolatum, based on the development of red color on treatment with a sulfuric acid solution of ferrous sulfate and ammonium sulfocyanate, and related the results of this test to shelf life. Stepina (*118*) determined, polarographically, nitrobenzene in oil that had been solvent refined with it. Adams and Castagne (*1*) studied the methods for determining furfural and confirmed that the colorimetric method based on reaction between furfural and aniline is specific for furfural; methylfurfural and hydroxymethylfurfural do not interfere, whereas they do interfere in bromine oxidation procedures. Hillyer and Deutschman (*49*) described a simple vacuum distillation, involving several successive evaporations with acetone, for determining polymer in furfural from furfural solvent refining or extractive distillation units.

Lykken (*83*) described a photometric method for determining color index of liquid petroleum products, to replace the A.S.T.M. Union colorimeter. Gold (*40*) employed the falling film type of molecular distillation apparatus, but at pressures much higher than used in molecular distillation, to distill organic compounds which decompose upon the relatively long exposure to temperatures needed for their distillation in ordinary apparatus. Booy and Waterman (*7*) applied the principle of the Salvioni balance to the molecular distillation of microquantities of polymeric substances, the balance pan being the evaporating surface which is heated by an infrared lamp. During the evaporation the weight of the pan is observed by its displacement on a millimeter scale. Moss *et al.* (*97*) determined phenols and other acids too weak to be titrated in aqueous medium, by titrating in anhydrous basic solvents such as ethylenediamine, with an even more basic titrant. In this system phenols and carboxylic acids behave analogously to carboxylic acid and mineral acid when titrated in water. Kreulen and Kreulen van Selms (*72*) described a modified hydroxylamine method for determining the carbonyl value of dark oils. Trillat and Brigonnet (*124*) applied interfacial tension to demonstrate that polar bodies are lost to metal surfaces over which a lubricating oil containing them flows, reaching a maximum beyond which further adsorption does not occur.

SPECIALTIES

Wiberley and Rather (*133*) reduced the A.S.T.M. method for determining oil in wax to the semimicro scale with an ordinary analytical balance and demonstrated that it is superior in economy of material and time without loss in precision. Kinsel and Phillips (*65*) described a photoelectric method for determining luster of petrolatums and waxes, expressed the result in luster index, and found it varied with penetration and inversely with melting point. Hampton (*44*) described a procedure for analyzing low temperature polymers by infrared absorption in carbon disulfide solution. Madorsky *et al.* (*85*) and Wall (*128*) applied mass spectrometry to the volatile product obtained on pyrolyzing polymerized unsaturated hydrocarbons and showed that this method serves to identify the polymers. Crippen and Bonilla (*20*) analyzed styrene polymers by depolymerizing at 300° to 400° C. at reduced pressure, nitrating the resulting styrene, and completing the determination spectrophotometrically at 365 millimicrons. Burkhard and Norton (*13*) identified the hydrocarbon substituents of organosilicon compounds and polymers by mass spectrometry of the cleavage products resulting from the action of sulfuric acid.

Thomas and Seyfried (*120*), Gifford *et al.* (*38*), and Langer and Fox (*77*) applied the mass spectrometer to the analysis of oxygenated compounds including alcohols, aldehydes, acids, esters, ketones, ethers, and water. Though the results are not as precise as the determination of hydrocarbons by mass spectrometry, they are nevertheless good. Coggeshall and Lang (*17*) discussed the effect of the solvent on the ultraviolet absorption spectra of unhindered and hindered phenols and showed that changes in the spectra occur when the solvent is changed. Maron *et al.* (*90*) in a study of conductometric and potentiometric titration methods for analysis of saponifiable acids, soaps, and acid-soap mixtures in aqueous isopropyl alcohol solvent found the conductometric method satisfactory for determination of the acids and titration with acid useful for the analysis of soaps. By an indirect titration procedure several constituents can be determined by a single titration.

POLLUTION

Corbett (*19*) determined sulfur trioxide in industrial flue gas by absorption in 80% isopropyl alcohol, which dissolves sulfur trioxide but very little sulfur dioxide. After reduction in volume by evaporation, the sulfate ion was determined turbidimetrically as barium sulfate. Key (*63*) determined the total sulfur, as barium sulfate, in stack gas by absorption and oxidation in hydrogen peroxide. Sulfur dioxide was determined by mass spectrometry. Special emphasis was given to correct sampling technique to prevent condensation losses between stack and sample collector.

An automatic and continuous titrating instrument, originally developed for determining mustard gas in air, was described by Shaffer *et al.* (*113*) and claimed suitable for determining hydrogen sulfide, sulfur dioxide, and acrolein, above 0.1 p.p.m. A portable kit for determining tetraethyllead in the atmosphere was described by Snyder *et al.* (*115*). The method is based on colorimetric comparisons involving reaction of tetraethyllead with iodine, finishing as the colored complex with dithizone. Lindsley and Yoe (*81*) described a thermostatically controlled indicating instrument based on temperature rise which occurs when carbon monoxide is oxidized over hopcalite, for warning when predetermined concentrations of carbon monoxide are present in the atmosphere. The instrument automatically actuates signaling devices. Landry (*75*) described a polarographic method for determining benzene in the atmosphere, involving nitration and selective oxidation to eliminate interference by toluene and xylene. Kirschman (*66*) determined the relatively nonvolatile liquid oil in oil-field waste waters by extraction with mixed hexanes, claiming better results than by metal salt flocculating procedures.

ELEMENTS

Basic nitrogen was determined by Wittmann (*135*) in hydrocarbon and coal-hydrogenation oils by titrating with perchloric acid in glacial acetic acid. Total nitrogen content of volatile organic compounds was determined by Buchanan *et al.* (*12*) by a semimicro-Dumas variation of the Niederl procedure. Hindin and Grosse (*50*) modified the Dumas combustion method for nitrogen by analyzing the gaseous product by mass spectrometry, using an inert gas as internal standard.

An adaptation of the Unterzaucher method, involving larger samples, was described by Dinerstein and Klipp (*25*) for the determination of oxygen in petroleum products. Results are given for samples containing from 0.15 to 26% of oxygen. Small amounts of oxygen in organic compounds were determined by Walton *et al.* (*129*) in another variation of the Unterzaucher method; the sample was pyrolyzed in an atmosphere of helium and the carbon monoxide collected in a colorimetric indicating gel after prior elimination of interfering pyrolysis products by passage through a trap cooled by liquid air.

Pepkowitz and Proud (*103*) described a universal gasometric micromethod for determining hydrogen in organic and inorganic compounds or metals by evolution of the hydrogen of the sample within a sealed iron capsule and diffusion of the liberated hydrogen through the walls of the capsule into an evacuated system where it is determined by subsequent combustion over copper oxide. Hindin and Grosse (*51*) described a lamp burning procedure for determining hydrogen in liquid petroleum fractions. Wear and Quiram (*130*) described several burners used for analysis of organic materials by lamp combustion, suitable for determining sulfur in aromatics, chlorine and bromine in gasoline, and carbon and hydrogen in certain organic substances. Ingram (*56*) studied the empty tube combustion micromethod of Belcher and Spooner, comparing it with the Pregl procedure for carbon and hydrogen and concluded that the former was more precise. Grosse *et al.* (*42*) determined oxygen, carbon, and nitrogen in organic compounds by elementary isotopic analysis by mass spectrometry after addition of known amounts of the heavy isotope of these elements to the sample. The method does not require quantitative determinations nor specificity of reaction.

Gassmann and O'Neill (*37*) described an emission spectrometric method using a porous cup electrode to determine phosphorus and metals in lubricating oils, claiming advantages over the Calkins and White procedure but principally the ability to use one analytical curve with different base oils. Parks *et al.* (*102*) reported on a comprehensive study of the errors and interferences in the application of the flame photometer to the determination of sodium and potassium.

SULFUR AND ITS COMPOUNDS

Ingram (*55*) described a new solid absorbent for sulfur dioxide, effective at room temperature and unaffected by carbon dioxide. Change in color from green to brown indicates exhaustion of the absorbent, which is prepared by heating a mixture of molecular quantities of silver oxide and silver metavanadate at 150° C.

Lane (*76*) found, from a study of the lamp method for determining total sulfur, that low and erratic results are obtained when uncombined sulfur is present in the sample; a Pyrex wick improves sulfur recovery; volatile organic compounds must be burned with a nonluminous flame for quantitative recovery of sulfur. Morris *et al.* (*95*) described a volumetric method for concentrations above 0.1% of elementary sulfur in aromatic hydrocarbons, based upon its reaction with sodium sulfite to form thiosulfate. Stragand and Safford (*119*) employed a modified gravimetric micromethod to determine sulfur in organic compounds without interference by nitrogen and halogens except fluorine. The sample is burned in oxygen over a platinum catalyst and the sulfur trioxide is retained on silver gauze, from which it is subsequently dissolved in water; the loss in weight is silver sulfate. The sulfur content of liquid hydrocarbons was determined by Kehl and Hart (*62*) in 10 minutes by x-ray absorption. Hydrogen sulfide in gases was determined by color intensity of the blue reaction product with *p*-aminodimethylaniline, by Fogo and Popowsky (*31*) and Kosior (*70*). Sease *et al.* (*112*) used iodoplatinate solution to determine organic sulfides in presence of polysulfides, by photometric measurement of blue starch-iodide. Reithel (*106*) observed a peculiar reaction between silver nitrate and organic trisulfides which serves to distinguish the latter from organic disulfides. Fogo and Popowsky (*32*) separated organic sulfur compounds from hydrogen sulfide and carbon oxysulfide by passing the gases through silica gel, which absorbs the organic sulfur compounds and permits the others to pass.

Mapstone (*86*) determined mercaptans (thiols) directly in gasoline by titration with silver nitrate, using sodium nitroprusside as internal indicator in the presence of an alkali and an amine. Tar bases do not interfere. Kolthoff and Harris (*69*) determined primary and tertiary mercaptans in mixtures by iodometric titration in presence of lead salts and silver nitrate titration in ammoniacal solution, both amperometrically. The mercaptans react with silver in the molar ratio of 1 to 1. In the titration with iodine, primary mercaptans react with 0.5 mole of iodine, whereas tertiary mercaptans react with 1 mole of iodine. The accuracy of the method is limited because some tertiary mercaptans react incompletely with iodine. Karchmer and Dunahoe (*60*) described a volumetric method for sulfides, thiosulfates, and sulfites in refinery spent caustic solution. Woodward (*136*) described a colorimetric method for small quantities of thiols, involving use of sodium nitrate in glacial acetic acid as reagent. Harnish and Tarbell (*45*) described quantitative methods for determining thiophenol, phenyl thiolacetate, diphenyl disulfide, and benzylphenyl sulfide, based on titration of thiophenol with alcoholic iodine in presence of pyridine; disulfide is reduced to thiophenol with zinc and acetic acid; phenyl thiolacetate is hydrolyzed to thiophenol with alcoholic alkali.

CATALYSTS

The analysis of fluid cracking catalyst by emission spectrometry, for traces of metal contaminants, was described by Gunn (*43*), who obtained results in fair agreement with those by chemical methods. Feldman (*30*) applied the porous cup electrode method to the direct spectrochemical analysis of aqueous solutions of many elements. Weaver and Brattain (*131*) employed lithium carbonate as flux and diluent to modify the effects of major constituents in inorganic samples for emission spectrochemical analysis.

MISCELLANEOUS

A method of determining relative color density of liquid products, involving photoelectric measurements, was described by Lykken and Rae (*84*), who claimed it particularly applicable to products whose spectral characteristics are like those of lubricating oils; the results are correlatable with phenomena such as oxidation degradation of petroleum products and for control of refining processes.

A torsional variable-speed viscometer for drilling muds was described by Bednarski (*6*). Elkarim (*28*) described a new type of viscometer employing a horizontal capillary tube with modified ends. Jacobs (*57*) described another horizontal capillary tube viscometer. Thompson (*122*), employing a falling sphere viscometer, described a method for indicating the passage of the sphere by the reference mark when employing opaque liquids. It depends on alteration of the inductance of a coil as the steel sphere passes through it. Franzen (*33*) described experiences with a continuously indicating viscometer in viscosity control of motor oil distillates. Zimmer and Beerbower (*139*) determined viscosity of grease by forcing it through a capillary tube under controlled conditions, the difference in pressures at inlet and outlet being a function of viscosity. Kinsel (*64*) described micro and semimicropenetrometers for determining the consistency of petrolatum and waxes. Lipkin *et al.* (*82*) described pycnometers for oil, a feature of which is a side arm that fills the pycnometer automatically by siphoning.

Rolfson *et al.* (*110*) described an automatic distillation unit which plots a complete distillation curve under the conditions of the A.S.T.M. procedure for gasoline, etc. Dixon (*26*), after considering many existing packings for laboratory fractionation columns, developed for analysis of complex hydrocarbon mixtures a gauze ring random packing which showed a fractionating efficiency of 84 theoretical plates per foot of height in some experiments, low holdup per theoretical plate, and low presssure drop.

Diehl and Hart (*24*) described a vacuum distilling column head which provided accurate vapor temperature measurement and regulation of reflux rate with a holdup of less than 0.1 ml. Doty (*27*) described a vacuum-jacketed vapor dividing reflux head employing two separate single-acting valves, one of which closes the reflux condenser while the other opens the product line and vice versa, whereby the liquid reflux never comes in contact with the product take-off valve and only saturated vapor passes the latter. Tunnicliff (*125*) described a gas thermometer for automatic control of temperatures down to −180° C., suitable for separation of gases by isothermal distillation. A semimicro molecular still described by Breger (*10*) employs the falling film principle.

In a patent to Schlesman (*111*), high frequency radiant energy was applied for the separation of materials of nearly the same boiling point but differing in their absorption of high frequency radiation. The component absorbing radiant energy has its energy level raised sufficiently to carry it over a partial condenser, whereas the other component condenses on it. Coffin and Funt (*15*) described fractional distillation experiments in which the conventional column packing was replaced by ultrasonic waves and concluded that sound waves probably improve fractionation by a mechanism different from that causing visual effect. Horsley (*53*) supplemented previous publications with tables of azeotropes and nonazeotropes.

Matheson and Eden (*93*) described the construction and performance of a differential manometer of high sensitivity whose sensitive elements are a pair of nesting diaphragms, displacement of which is measured by resistive unbalance of an unbonded electrical displacement gage to which the diaphragms are attached. Zaukelies and Frost (*137*) described a pen and ink recording differential refractometer as sensitive as an interferometer and claimed suitable for following fractional distillation or adsorption fractionation. Zuidema and Pilz (*140*) studied the validity of the correction factor applied to the interfacial tension of water against organic liquids heavier than water and concluded that the corrected ring method for determining interfacial tension appears to be equally applicable whether the ring is being pulled upward from water to an organic liquid lighter than water or pushed downward from water to an organic liquid heavier than water. Kitson *et al.* (*67*) described a modified ebulliometer for molecular weight determinations by the method of Menzies and Wright, claiming a precision of about 1%. Breazeale (*9*), concluding that viscosity gradient–viscosity relationship should be related to the molecular weight distribution of macromolecules, suggested a method for determining molecular weight distribution of high polymers from viscosity gradient–viscosity data.

Evans *et al.* (*29*) reported irregularities involving increases in freezing point instead of decreases upon introduction of small amounts of one hydrocarbon into another, due to solid solution effect. Some solutes produced only a fraction of the normal lowering. This is of importance in connection with purity determinations based on cryoscopic data. Levin (*79*) presented a review of applications of microchemistry in the petroleum industry. Zerwekh (*138*) described a device for converting infrared intensity–wave-length curves to per cent transmission curves. The incident energy and transmitted energy curves are obtained in conventional manner, except that they are superimposed on the same chart which is then placed in another instrument and the curves are traced simultaneously by hand with two pointers placed on a single track. Hughes *et al.* (*54*) reviewed applications of x-ray diffraction methods to rapid analysis in the petroleum industry. Roberts and Johnsen (*108*) gave the mass spectra of 53 organic compounds, including many hydrocarbons.

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PHARMACEUTICALS AND NATURAL DRUGS

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THE analysis of pharmaceuticals and natural drugs has received considerable attention in the published literature during the 12-month period following the initial review paper which appeared as a part of the Annual Review of Analytical Chemistry last year (*117*). This review covers as nearly as possible those contributions which appear to be of value to the pharmaceutical analyst, but no attempt has been made to present a critical analysis of these suggested procedures. As a basis for further discussion, the various analytical procedures used in the pharmaceutical field have again been divided into three broad classifications: Chemical Methods, Physicochemical Methods, and Physical Methods.

CHEMICAL METHODS

ALKALOIDS AND RELATED SUBSTANCES

Bismuth iodide and antimony iodide in ether (*269*) are reported to give both qualitative and quantitative precipitates with alkaloids, salts of alkaloids, and pseudoalkaloids. Levo-noradrenaline

(*84*) may be used to identify the sympathomimetic ergone, and according to a British patent (*226*) derivatives of lysergic and isolysergic acid may be separated.

Two modifications of official methods for the assay of belladonna preparations have been reported. One method suggests the use of enzymatic digestion (*266*) to remove interfering substances, while the other proposes the substitution of a sintered-glass funnel (*210*) for the Soxhlet apparatus in the extractive procedure. The use of the enzymatic digestion step has also been suggested in the assay of colchicum corm and seed (*7*) preparations.

A new approach to the analysis of cinchona and nux vomica (*288*) is described, in which the alkaloids are separated from the plant constituents by microsublimation from the powdered drug which has been treated with sodium carbonate. The determination of barbiturates, their sodium salts, and other organic salts by titration procedures in which potentiometric means of determining the various end points are utilized is discussed by Waters *et al.* (*271*). These procedures are reported to be of particular value in colored solutions where the use of indicators would be limited.

A critical and comprehensive review of the methods used to standardize curare (*46*) and other curarizing substances has been published, and detailed assay procedures (*6*) for yohimba, jaborandi, ephedra, and ephedrine in nasal sirups have been discussed and evaluated. In the assay of theobromine (*19*) in theobromine and sodium salicylate a volumetric acidimetric method is suggested in place of the present National Formulary gravimetric assay. The behavior of caffeine, theobromine, and theophylline, when treated with Mayer's reagent (*217*) is discussed, as are various studies on the chemical determination of acetanilide (*31*).

ANTIBIOTICS

Potassium ferricyanide as an oxidizing agent and ceric sulfate as a volumetric standard (*118*) provide the basis for a method similar in design to the present iodometric procedure for the assay of penicillin. Comparative results with bioassays, it is reported, show better agreement for the ferricyanide method than for the iodometric procedure. Another method for the assay of crystalline penicillins, in which use is made of partition chromatographic procedures (*113*) where 30 *N* sulfuric acid or a mixture of concentrated sulfuric acid and phosphoric acid absorbed in Celite 545 is the stationary phase and benzene is the mobile phase, is discussed. The "R-group acids" present after hydrolysis are serially eluted and titrated. The method is not applicable to estimation of penicillin X. The formation of an acidic group, when penicillin is treated with hydrogen peroxide and excess alkali, forms the basis of a method of assay reported by Wise and Twigg (*282*).

The chemical analysis of bacitracin (*63*) and the amperometric microtitration of streptomycin and dihydrostreptomycin (*57*) are also reported.

METALLIC IONS AND RELATED SUBSTANCES

Arsenites (*145*) may be determined by iodometric titration in the presence of various buffering agents so long as the final pH is in the range of 6.9 to 10.6. Microquantities of bismuth (*150*) may be determined in various ways. Two methods are described, which are based on the precipitation of the bismuth (*236*) as the iodate or chromate followed by iodometric determination of the excess iodate or chromate.

A direct potentiometric titration procedure is recommended for the determination of calcium gluconate (*128*). What is claimed to be a rapid combustion method (*56*) for carbon and hydrogen in organic compounds, which appears to have the same order of accuracy that the Pregl method permits, is reported, as is a new volumetire method for the determination of iron (*2*).

The halogens as a class have received a considerable amount of attention lately. Methods for separation (*88*) of bromides, chlorides, and iodides in pharmaceuticals as well as reviews (*18, 144*) of the numerous macro and micromethods of determining halogens have been reported. Chlorine, hypochlorite (*87*), iodoform (*76*), and iodine (*111*) in thyroid have all received attention in the literature, and various procedures are outlined.

Qualitative tests for mercury (*238*), as well as a quantitative (*21*) method which uses a sulfuric acid–potassium permanganate procedure to destroy organic matter with subsequent titration of the mercury with potassium cyanate, have been reported. Sodium (*259*) in sodium citrate may be determined by direct titration using methyl orange as the indicator, while sodium and potassium (*134*) are separable if one employs ion exchange resins. Amberlite IR-100 is the particular ion exchange resin used by the authors.

Identification tests for sulfur (*37*) in organic compounds are possible by reducing the sample in a capillary tube with the aid of heat, anhydrous potassium carbonate, and powdered magnesium. The hydrogen sulfide evolved may be tested for with filter paper impregnated with 0.1 *N* lead acetate containing a few drops of acetic acid. The sulfur (*178*) of the CS group in certain aromatic thioureas changes almost completely to silver sulfide when treated with excess ammoniacal silver nitrate, and sulfoxylate sulfur (*17*) can be determined by acidic iodine oxidation.

VITAMINS

A new chemical method for the estimation of ascorbic acid has been described by Huelin (*123*), who has employed observations of the rate of condensation of ascorbic acid with formaldehyde as a means of estimating the amount of "apparent" ascorbic acid present. Goldblith and Harris (*95*) have compared the indophenol titration with the dinitrophenylhydrazine method of Roe *et al.* (*216*).

Seaman *et al.* (*232*) have described a gravimetric method for the determination of certain choline salts by precipitation of the cobalt chloride complex from ethanol, in which the complex is sparingly soluble.

GENERAL

Reports of the various methods for determining aldehydes (*109*) particularly in volatile oils, acetaldehyde, and acetone (*247*), and the chemical characteristics of aerosporin (*43, 131*) and the determination of arginase (*212*), tryptophan (*242*), β-glucuronidase (*165*), and nitrogen (*279*) content of proteins are all to be found in very recent publications. The effects of various catalysts and modifications of the original Kjeldahl method for the determination of nitrogen (*114, 180, 199*) are also discussed.

A method for determining the proteolytic activities of enzyme preparations uses casein (*50*) as a substrate, while pepsin may be determined by a method utilizing coagulated egg yolk (*225*).

Under proper conditions the methylamine reaction can be used for the detection of lactose (*182*). Naphthalene (*86*) may be determined by reduction with zinc dust and by the sulfite method. Small quantities of water (*192*) in organic solvents will precipitate lead dioxide from a solution of lead tetraacetate. As little as 1 microgram of carbonate (*61*) may be detected with barium hydroxide under specific conditions.

Shaefer (*234*) has described a distillation procedure by which 0.0 to 2.0% of ethyl ether in ethyl alcohol may be determined. Azides (*110*) may be determined by precipitation and subsequent titration with absorption indicators and Langenau (*146*) has published a procedure for determining phenols in thyme oils.

PHYSICOCHEMICAL METHODS

ALKALOIDS AND RELATED SUBSTANCES

At least three fluorometric (*153, 175, 189*) procedures for the determination of adrenaline have been proposed in addition to colorimetric (*33, 75*) methods not only for adrenaline but also for arterenol (*11*) in adrenaline.

In the field of narcotics microchemical reactions for the identification of metopon (*85*), dolophine (*229, 272*), cocaine (*286*), and copalquin bark (*230*), and colorimetric assay procedures for morphine (*60, 71, 105*) have received the attention of analytical chemists and their results have been made a part of the current literature.

Antipyrine may be determined colorimetrically by coupling with dimethylaminobenzaldehyde (*69*) or by forming 4-nitrosoantipyrine (*32*) and subsequent spectrophotometric assay. Nicotine (*284*) may be determined spectrophotometrically also, and conessine (*195*) may first be precipitated as the silicotungstate and then determined colorimetrically.

A study of the quantitative estimation of digitoxin and digitoxigenin with the Baljet (*20*) reagent has been reported along with a photometric evaluation of cardiac glucosides (*268*) and a review article on the estimation of the digitalis and strophanthus glycosides (*38*). Bersin (*22*) has described a colorimetric method for the quantitative estimation of *Uzara* glycosides which utilizes 2,4-dinitrochlorobenzene in alkaline medium to produce a blue color which is stable for about 20 seconds. Glycosidic methoxyl groups have been determined by hydrolysis with strong acid, distillation and oxidation of the methanol formed, and colorimetric determination of the resulting formaldehyde (*119*).

The antihistaminic drugs have provided the chemists considerable subject matter for developing identification (*107, 108*) tests and quantitative (*130*) assay procedures. Those antihistaminics which are 2-substituted pyridine derivatives have been reported by Perlman (*191*) to form fluorescent compounds capable of quantitative measurement by means of a modified cyanogen bromide reaction. The barbiturate derivatives are another group of drugs that have been the subject of several reports on identification (*157*) and quantitative (*161, 254*) estimation.

A qualitative scheme (*122*) for the characterization and identification of the eleven local anesthetic drugs of the benzoic ester group at present commercially available in this country is described and discussed. A simple quantitative spectrophotometric method (*14*) for the determination of procaine and *p*-aminobenzoic acid in the presence of each other is reported to have a sensitivity of 2.5 micrograms.

Benzedrine, dexedrine, ephedrine, racephedrine, propadrine, and paredrine may be identified by preparing the corresponding diliturätes (*198*) (nitrobarbiturates). Strychnine (*54*) may be determined colorimetrically by its reaction with ceric sulfate in the presence of sulfuric acid. The determination of *d*-tubocurarine chloride (*141*) by direct ultraviolet absorption as well as colorimetrically by preparing the reineckate complex is reported.

ANTIBIOTICS

Notes are given by Roux (*219*) on the use of the coloration with sodium nitroprusside in acetic acid for the detection of penicillins. Boxer *et al.* (*29*) utilize the chloroform extraction of benzylpenicillin from an aqueous solution of pH about 2 to separate the substance from interfering phenyl monocarboxylic acid derivatives and then develop a color according to the Kapeller-Adler reaction. The hydroxylamine method (*112*) of assay of penicillin has been improved in accuracy and convenience, by extracting the resulting complex into butyl alcohol before color measurement.

A colorimetric method for the determination of streptomycin B which uses Morris' reagent (0.2% anthrone in 95% sulfuric acid) is described by Emery *et al.* (*82*). The results obtained by this method appear to be in accord with those calculated from chemical and biological assays. A chemical method (*190*) for the determination of streptomycin B in purified preparations based on the color formed with carbazole in sulfuric acid solution is described. Roux (*220*) has enumerated a series of color reactions for streptomycin and has considered the possibilities of adapting some for colorimetric determination of this antibiotic.

CHEMOTHERAPEUTIC AGENTS

The reaction of certain 2-substituted pyrimidines, including sulfadiazine (*237*), with 2-thiobarbituric acid in acid medium can be used for the quantitative estimation of these substances. Lapière (*147*) has discussed the Parri reaction and the sulfonamides, and the optical crystallographic properties (*42*) of some sulfonamides and their derivatives and the identification (*121*) of the clinically important sulfonamides have received considerable attention by various workers. A colorimetric method for determining homosulfanilamide has been described by McChesney *et al.* (*156*).

METALLIC IONS AND RELATED SUBSTANCES

Boron (*222*) compounds may be analyzed colorimetrically when as little as 0.5 to 1.5 micrograms of boron are present. Small amounts of copper (*276*) (0 to 15 p.p.m.) in water can be determined with considerable accuracy utilizing the colored complex formed with dithio-oxamide. Malonic acid may be added to serve both as a buffer and to sequester interfering ions. Another method for copper (*214*) is based on the extraction of copper carbamate with isoamyl alcohol. Cobalt chloride (*13*) in ethyl alcohol may be determined spectrophotometrically in a concentration range of 100 to 400 p.p.m. Two to 100 micrograms of gallium (*78*) in biological material can be determined colorimetrically.

Inorganic and organic materials containing iodine (*103*) in the range of 1 to 14 micrograms can be analyzed by a spectrophotometric procedure which utilizes the color developed by the starch-iodine chromogen. For the determination of iodine (*58*) in blood, Connor *et al.* have developed a method which appears to answer the requirements of the clinical laboratory. A colorimetric method is described for the determination of iron (*132*) and copper in which organic matter is destroyed by rapid wet ashing with a mixture of sulfuric, perchloric, and nitric acids using vanadium as a catalyst. Special precautions against dust and reagent contamination are necessary.

Lead (*49*) in biological material may be extracted at a high pH and determined by dithizone. Traces of mercury (*126, 176, 188, 264*) may be determined in various ways, while sodium (*97*) may be determined colorimetrically by a method based on the precipitation of sodium as the triple salt of uranium and zinc acetate and intensification of the color of the uranium ion with hydrogen peroxide in alkaline solution. Heavy metals (*155*) may be determined in somewhat colored solutions by compensating for the color in the solutions through the use of multiple compartment observation tubes. Zinc in pharmaceutical preparations and similar products may be determined by various dithizone extractive procedures (*5, 262, 263*).

VITAMINS

The reaction of vitamin A with certain acidic reagents to produce colored products has been made the basis of identification tests by Carreyett (*40*), who used ferric chloride in concentrated hydrochloric acid, and Robin (*213*), who employed the Liebermann-Burchard reagent. A colorimetric method for the vitamin utilizes bentonite activated with dilute hydrochloric acid, the preferred liquid phase being chloroform (*265*). Rice *et al.* (*206*) have discussed the present status of the antimony trichloride procedure. Practically quantitative separation of vitamin A from its oxidation products and from carotenoids is reported by Narod and Verhagen (*174*), using a magnesia-Celite adsorption column. Paper chromatographic techniques have been applied to the separation of vitamin A in mixtures by using filter paper impregnated with alumina (*65*). The paper is immersed in aluminum sulfate solution, then dipped in ammonium hydroxide solution, washed thoroughly, and drained. The dried, impregnated strip is suspended in an atmosphere of nitrogen during development of the chromatogram with a light (80° to 100°) petroleum fraction. The antimony trichloride reagent is sprayed on the strip to locate zones.

Developments of interest in the assay for thiamine have been confined largely to modifications of the thiochrome procedure. Mawson and Thompson (*162*) have suppressed the thiochrome fluorescence with hydrochloric acid treatment of the isobutyl alcohol extract in order to determine extraneous fluorescence. Evidence has also been presented that the addition of small amounts of gelatin added to thiamine solutions stabilizes the fluorescence readings (*44*). The testing of various steps in the thiochrome procedure has demonstrated that the source of greatest error is in the oxidation-extraction step (*53*). Rigid standardization of this step is recommended. Ridyard (*211*) has observed that isobutyl alcohol extracts of thiochrome are stable for an hour or more if kept in the dark. Patrick and Wright (*187*), utilizing mercuric oxide as oxidant, have determined thiamine in pharmaceutical products by making a final reading in aqueous acetone solution. These workers claim that an aqueous solution of 1-methyl-5-aminoacridine hydrochloride is more stable than the usual quinine sulfate working standard.

Runti (*221*) has described another coupling procedure for the estimation of thiamine, employing a diazotized amine.

Using either acidic or basic water-saturated butanol as developer, Hais and Pecakova (*106*) have separated riboflavin with paper chromatographic techniques. Modifications of the fluorometric method for the estimation of riboflavin include use of the fluorescence quenching effect of relatively strong acid concentrations for the determination of blank fluorescence (*100, 101*). Kodicek and Wang (*143*) have described a fluorometric procedure for riboflavin in certain natural materials, in which it is reported that adsorption techniques are not necessary for quantitative determinations of the amount of riboflavin present.

Smith (*239*) has described the color tests used to identify cobalt in vitamin B_{12}, together with a colorimetric quantitative procedure for cobalt employing 1-nitroso-2-naphthol.

The differentiation of L-ascorbic acid from D-isoascorbic acid has been facilitated through the observation that the former reacts with nicotinic acid to form a characteristic yellow complex (*274*). The color formed by reaction of silicotungstic acid with ascorbic acid has been utilized (*15*) in a colorimetric method for the estimation of the vitamin. The color fades rapidly, but sulfites, bisulfites, and hyposulfites are reported not to interfere.

A colorimetric method for the estimation of vitamin D, involving application of the antimony trichloride reagent and guaiacol, is reported by Diemair and Manderscheid (*72*).

Of considerable interest in regard to assay methods for the tocopherols is the recent work of Quaife *et al.* (*201–203*), in which the nitroso derivatives of β-, γ-, and δ-tocopherol have been formed and have been found to be satisfactory for the quantitative spectrophotometric estimation of these isomers. The nitroso derivatives of the isomers can be separated chromatographically. Alpha-tocopherol does not react to produce a nitroso derivative.

Folic acid has been determined colorimetrically (*93*) by a diazotization procedure, polarographically (*79, 159*), and fluorometrically (*4, 9, 267*) by oxidation. The fluorometric procedures appear to be the most specific.

Various physical characteristics of nicotinic acid, including the ultraviolet absorption spectrum, have been described recently (*124*). Modifications of the cyanogen bromide method have also appeared (*66, 140*). Kodicek and Chandhuri (*142*) have modified a fluorometric procedure for nicotinamide originally outlined by Scudi (*231*) to permit the entire reaction to take place in aqueous solution. Most interfering substances are removed by mild alkaline pretreatment of the sample. An internal standard compensates for the inhibiting effect of any nicotinic acid present.

GENERAL

Considerable attention has been directed to the separation of amino acids during the past year—both the naturally occurring mixtures from protein hydrolyzates and synthetic mixtures. Stein and Moore, in a series of papers (*168, 244, 245*) describe the chromatography of some protein hydrolyzates on starch columns and a photometric ninhydrin method for the determination of the separated acids. This same separation procedure has also been used for the separation of thymine, uracil, adenine, and some other purines and pyrimidines (*62*). Paper chromatography has been used by Dent (*67*), Bull *et al.* (*34*), Block (*25*), and Martin and Mittelmann (*160*), while Consden *et al.* (*59*) utilize an anion exchange resin (Amberlite IR4B) for certain amino acid separations. Kibrick (*139*) employed Permutit for the separation of basic amino acids.

A new color reagent for amino acids is *peri*-naphthindan-2,3,4-trione hydrate (*167*); the mechanism of the reactions appears to be similar to that of ninhydrin. Procedures for the estimation of individual amino acids include a colorimetric method for thyroxine which involves reaction with diazotized *N'*-diethylsulfanilamide (*281*); a reaction of perchloric acid with tryptophan (*250, 251*) has been used for identification purposes. The quantitative estimation of tryptophan has been accomplished fluorometrically (*98*) and by reaction with *p*-dimethylaminobenzaldehyde (*241*) in both hydrolyzed and unhydrolyzed proteins.

The increasing use of *p*-aminosalicylic acid in the treatment of tuberculosis has prompted several reports (*70, 248, 252*) of new modifications for the estimation of small quantities of this drug.

New tests and quantitative procedures for carboxylic acids include a new color reaction of acetic acid and acetates (*185*) with phenylhydrazine and an oxidizing agent; citric acid can be determined by formation of the highly fluorescent ammonium citrazinate (*148*). The method is applicable to quantities of the compound in the range of 10 to 75 micrograms. Moyle *et al.* (*169*) and Peterson and Johnson (*193*) describe the separation of various fatty acids by partition chromatography.

A general qualitative test for aliphatic alcohols involving the use of the vanadium-oxyquinoline complex has been described (*36*), but the sensitivity is rather low. Certain α,β-unsaturated aldehydes and ketones react with *m*-phenylenediamine to form colored products which can be estimated spectrophotometrically (*273*). Most simple aromatic and aliphatic aldehydes do not interfere. A relatively sensitive color reaction of certain esters of *p*-hydroxybenzoic acid with *m*-nitrobenzaldehyde has been described (*68*); the free acids do not give the colored reaction product. Witter, Snyder, and Stotz (*283*) describe a colorimetric determination of certain β-diketones by condensation with *o*-phenylenediamine.

An extension of the many uses of the Folin-Denis phenol reagent involves its use in the colorimetric determination of capsaicin (vanillyl amide of isodecenoic acid) by North (*179*). A modification of the method of White and Rolf (*278*) for the determination of diodrast (diodone) has eliminated the need for special apparatus (*26*).

Borntraeger's reaction has been utilized in the development of colorimetric and fluorometric methods of assay of Alexandria senna leaves (*52*) and certain anthraquinone drugs (*51*).

Much emphasis has been placed on the separation, identification, and estimation of the various estrogenic and other hormones during the past year. Umberger and Curtis (*260*) have described the chromatographic separation of the *p*-phenylazobenzoyl esters of the natural estrogens; the method (*261*) has been used for the estimation of estrone and α-estradiol in mixtures in less than 1-mg. amounts.

Nielsen (*177*) utilized a reaction of testosterone with concentrated sulfuric acid followed by dilution with alcoholic sulfuric acid for a colorimetric assay, and Hilmer and Hess (*115*) determined this hormone spectrophotometrically as a solution of the

2,4-dinitrophenylhydrazone after chromatographic separation from the corresponding androsterone derivative. Munson *et al.* (*171*) have described a colorimetric method for dehydroisoandrosterone. The separation and estimation of adrenal cortical hormones have been discussed in some detail by Staudinger and Schmeisser (*243*). These workers used successive solvent partitions for separation; a phosphomolybdic acid reagent was employed in the colorimetric assay. The absorption spectra of antimony trichloride–steroid reaction products has been the subject of an investigation by Mueller (*170*). The hydrazones of certain ketosteroids have been chromatographed on paper, followed by a color reaction with iodoplatinate or iodobismuthate (*287*). The characteristics of certain crystalline perchloric acid and hexafluorophosphoric acid salts of sterols have been reported by Lange *et al.* (*145*).

The applications of physicochemical methods to the determination of inorganic ions of pharmaceutical interest include a procedure for the estimation of nitrites in the presence of nitrates by interaction with thiourea in the presence of boric acid (*35*). The thiocyanate formed is determined colorimetrically after addition of ferric ion.

Golden (*96*) has utilized the oxidation of ferrous ion to ferric ion to determine the amount of peroxide in petrolatum. Primary and secondary aliphatic nitro compounds have been assayed colorimetrically by Turba and Haul (*256*) by reaction with diazotized sulfanilic acid and nitrous acid, respectively.

Analytical methods for various carbohydrate substances are those of Dische *et al.* (*73*), for certain hexoses which react characteristically with cysteine hydrochloride in strong sulfuric acid; of Englis and Miles (*83*), which makes use of the difference in oxidation rate between levulose and dextrose for the determination of levulose with the Folin-Denis reagent; and of Smith and Stocker (*240*), which employs a dinitrosalicylic acid reagent for the estimation of the amount of reducing sugars produced as a measure of invertase and β-glycosidase activity. New color methods for the determination of inulin are described by Roe *et al.* (*215*) and Cargill (*39*). Among the macromolecular carbohydrates, Meyer *et al.* (*164*) have discussed comprehensively the structure and analysis of starch solutions and pastes.

Certain thiols have been found to react with sodium nitrite in acid solution to produce a red color; a colorimetric method for thiols utilizing this phenomenon has been described by Woodward (*285*). The liberation of thiocyanate in the interaction of 1,2-dithiols with cyanogen chloride has enabled Aldridge (*3*) to determine such compounds as BAL by this reaction. Derivatives of thiouracil have been determined colorimetrically with Grote's nitroprusside reagent (*92, 120*). A color reaction of urea with diacetyl in the presence of an aromatic amine has been made the basis of an analytical method for the estimation of urea (*277*), and a transient color reaction of urethane with furfural in strong acid has been described (*218*).

Some physical and chemical constants of a volatile oil isolated from *Pycnanthemum pilosum* Nutt have been described recently by Chilquist *et al.* (*48*).

PHYSICAL METHODS

ALKALOIDS AND RELATED SUBSTANCES

Polarographic methods of analysis of berberine, hydrastine, cotarnine (*227*), and colchicine (*228*) appear to be available for these alkaloids. The characteristic absorption of caffeine (*127*) in the region of 272 mμ may be utilized to measure its concentration in various preparations, and the ultraviolet absorption of pyranisamine maleate (*8*) offers a convenient method for determining its concentration. Several analytical methods for the estimation of barbiturates (*28, 94, 270*) utilize their absorption characteristics in the ultraviolet region along with the optical crystallographic data (*41*) of Alphenal, Cyclopal, Delvinal, Evipal, Mebaral, Ortal, Pentothal, Phanodorn, Seconal, and Sigmodal.

Identification (*45*) of vegetable drugs may be accomplished by exposing the powdered drug to ultraviolet radiation. Benzedrine and dexedrine (*135*) may be differentiated according to the microcrystallographic data made available by Keenan, and various sympathomimetic amines (*136*) may also be identified from information published by this same author. The polymorphic forms of ouabain (*137*) serve as identification characteristics of this drug, as does the crystal formation of amidone (*134*) with various reagents.

The ultraviolet absorption characteristics of theophylline, theobromine, and caffeine (*258*) serve as a means of determining the dissociation constants of each. Hydrastis (*163*) may be analyzed by a method which is based on the adsorption of the alkaloids on Florisil columns. Hydrastine is selectively eluted with ammoniacal alcohol and determined by a spectrophotometric procedure. Ion exchange resins (*129*) have been utilized for the quantitative analysis of various alkaloidal salts, the ion exchange resin Amberlite IR4B is utilized to remove the anions present and the free alkaloid is determined in the effluent.

ANTIBIOTICS

The ultraviolet absorption curve of crystalline antimycin A (*80*) together with optical rotation, melting point, and qualitative functional group tests is now available. The same information is also reported for chloromycetin (*204*) by the workers who synthesized this antibiotic.

The separation of various penicillins by chromatographic procedures (*27, 151, 253*) offers a variety of approaches to the problem of isolating a particular penicillin. At least two spectrophotometric procedures for penicillin G (*55, 152*) utilize the ultraviolet absorption characteristics of this compound as a basis for estimating its potency. Still another method describes the use of infrared (*91*) analysis as a means of determining the quantity of crystalline penicillin G present in a given compound. Procaine (*224*) in procaine penicillin G may be determined by ultraviolet absorption. Results of this type of determination compare very favorably with chloroform extraction–titrimetric methods.

Some work on the separation of streptomycins has been published. One method utilizes a countercurrent distribution system and the Craig machine (*197*), with subsequent conversion of the streptomycin to mannitol and ultraviolet measurement. Another method makes use of the continuous countercurrent extraction technique for binary separations (*181*).

CHEMOTHERAPEUTIC AGENTS AND METALLIC IONS

The physical properties (*223*) of sulfanilamide, sulfaguanidine, sulfapyridine, sulfadiazine, sulfathiazole, sulfamethylthiazole, and their corresponding picrates and acetates have been described. This is suggested as the best method of identification of these compounds. The analysis of mixtures of sulfadiazine and sulfathiazole, utilizing ultraviolet absorption techniques, is described by Banes (*16*).

In 1.0 *N* hydrochloric acid thiomersalate (*184*) gives a well defined step, −0.48 volt versus the calomel electrode when assayed polarographically. The use of this method is suggested for the determination of thiomersalate in vaccines and pharmaceutical preparations.

VITAMINS

The chromatographic separation of vitamin A from materials which interfere in the spectrophotometric assay has been recommended in several recent papers. A column of iron particles of uniform (70μ) size has been reported to adsorb vitamin A from petroleum ether solution (*233*); the vitamin is eluted with aqueous alcohol. Gridgeman *et al.* (*102*) have used activated alumina as adsorbent for the vitamin. Comparison of the spectrophotometric method—both direct and after saponification and extraction of the nonsaponifiable fraction—with the glycerol dichlorohydrin, antimony trichloride, and chromatographic procedures has been made by Chilcote, Guerrant, and Ellenberger (*47*). These workers compared results obtained on 28 fish oils of both high and low potency. In general, the color methods utilizing the nonsaponifiable fraction gave results which approximated the bioassay most closely; however, the conversion factors used with the spectrophotometric assay were 2000 and 1925. A report on vitamin A by Wilkie (*280*) recommends utilization of the 340 mμ reading of the absorption curve with a conversion factor of 2375; less interference of nonvitamin A absorbing materials in this range is claimed. Use of the Morton-Stubbs correction with a conversion factor of 1800 has been proposed (*257*). In an effort to extend the use of the Morton-Stubbs correction in order to prove or disprove its validity, Oser (*183*) has described a simplified form of the correction; it can be used for cases in which it is not necessary to plot the irrelevant absorption.

A description of the technique of isolation and of the physical and chemical properties of vitamin A_2 is reported by Shantz (*235*).

The use of a synthetic phenol sulfonic acid cation exchange resin in the separation of riboflavin has been recommended (*90*). The vitamin is eluted from the resin with pyridine–acetic acid mixture. The ultraviolet absorption characteristics of riboflavin have been redefined by Adamson (*1*).

The past year has witnessed the appearance of commercially available crystalline vitamin B_{12}. In a series of four papers (*30*, *207–209*) Rickes, Brink, Koniuszy, Wood, and Folkers have described many of the physical and chemical properties of this substance. The identification of vitamin B_{12a} together with some of its properties has also been reported (*133*). Pierce, Page, Stokstad, and Jukes (*194*) and Ellis, Petrow, and Snook (*81*) have reported absorption spectra and extinctions for vitamin B_{12b}.

The crystallographic properties of pure ascorbic acid have been described (*10*). An examination of the infrared absorption characteristics of compounds related to ascorbic acid indicates that the analysis of certain mixtures is possible and more satisfactory than by present chemical methods (*255*).

An interesting procedure for the separation of free choline from its water-soluble modifications involves adsorption of the free base on silica gel (*77*).

As a possible aid in the physical determination of vitamin D in the presence of vitamin A, the effect of addition of maleic and citraconic anhydride on the absorption of these vitamins has been studied (*173*). Maleic anhydride was observed to have no effect on vitamin D, but reduced the absorption of vitamin A to less than 10% of its original value. Infrared absorption methods have been used to determine vitamin D_2 in irradiation products of ergosterol (*196*); the method is relatively insensitive.

The ultraviolet absorption curves of pure rutin and quercetin have been described (*246*); the spectrophotometric method described utilizes $E^{1\%}_{1\ \text{cm.}}$ at 347, 362.5, and 375 mμ. A quantitative quercetin determination is made. Porter (*200*) has proposed a colorimetric method for rutin based on the yellow color ($\lambda_{\text{max.}}$ = 413 mμ) of the aluminum chloride–rutin complex.

GENERAL

The differentiation of leucine and isoleucine and of their acetyl derivatives in protein hydrolyzates by means of their infrared absorption spectra has been reported by Darmon *et al.* (*64*). The selective adsorption of glutamic and aspartic acid from a group of fifteen amino acids has been demonstrated by Tarte (*249*), using a barium sulfate column. If the column is activated with barium nitrate, the adsorbent no longer fixes glutamic acid. Considerable chromatographic resolution of enzymes is claimed by Mitchell, Gordon, and Haskins (*166*) with the filter paper "chromatopile" developed in their laboratories. Wesselman and Hilty (*275*) have described a rapid turbidimetric method of estimation of pepsin activity, using a crystallized egg albumin substrate and photometric measurement of residual turbidity.

Analytical procedures for the estimation of the salts of certain organic acids are reported by Bjorling (*24*), who has utilized an ion exchange resin to convert the salts of citric, tartaric, lactic, gluconic, and other acids to a titratable form. The method is not satisfactory for salts of propionic or benzoic acid. A detailed description of the physical and chemical properties of *p*-aminobenzoic acid and its sodium salt has been published recently (*138*).

LeRosen and May (*149*) have attempted to correlate the characteristics of some aliphatic aldehydes with their chromatographic properties on silicic acid.

A spectrophotometric method for the estimation of 4-hydroxycoumarin in certain biological fluids is reported by Axelrod *et al.* (*12*).

Using a supporting electrolyte of tetraethylammonium hydroxide Hilton (*116*) has determined digitoxin polarographically. The average half-wave potential is −1.96 volts. The plot of concentration against diffusion current of samples extracted from blood is not linear.

Physical methods applied to the determination of estrogenic compounds include ultraviolet absorption studies (*89*) and a polarographic method involving reduction of the nitroso derivatives of some of the synthetic estrogens (*104*). Polarographic studies on diethylstilbestrol indicate that it is not oxidized or reduced polarographically, but that it does suppress the oxygen maximum. This latter characteristic has been utilized in a quantitative manner (*23*). The method of Carol *et al.* for the determination of estrone, equilin, and equilinen by infrared spectrophotometric measurements has been extended and subjected to mathematical treatment (*172*). Goulden and Warren (*99*) have presented data on the polarographic characteristics of 37 compounds of the stilbene and stilbestrol series.

Microscopic methods for the identification of organic compounds have been applied to three groups of 87 closely related compounds (benzoic acid and barbituric acid derivatives and sulfonamides) by Reimers (*205*); this worker employed standard glass powders for the determination of the refractive index of these compounds at their melting point.

The chromatographic behavior of 22 sugars and sugar derivatives on filter paper strips has been investigated by Partridge (*186*). Ikawa and Niemann (*125*) have extended their observations in regard to the spectrophotometric characteristics of certain aldoses and ketoses in 79% sulfuric acid. The densities and refractive indexes of lactose solutions are reported by McDonald and Turcotte (*158*). A study of the refractive indexes of various gums, resins, and waxes at and above their melting points has been made by Dobran, Acker, and Frediani (*74*).

CONCLUSIONS

Throughout the past year there has been definite evidence of increased use of separation techniques rather than selective reactions as a means of increasing the specificity of analytical procedures. Among the newer methods, chromatographic separations have gained prominence. The various ion exchange materials appear to yield the most precise results, whereas separations by other types of adsorbents—including paper—still leave something to be desired so far as precision is concerned.

Countercurrent distribution systems as aids in separation techniques have achieved new analytical significance, particularly in the field of antibiotic analysis. Further refinement of apparatus promises extension of this type of separation method.

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NATURAL AND SYNTHETIC RUBBERS

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This paper is the second of a series of review articles to appear in this journal on analytical methods pertaining to natural and synthetic rubbers. The first review (*27*) covered the period from about 1944 until the latter months of 1948, and dealt only with chemical methods. The present review, which covers the past year, takes up where the previous one left off and includes articles appearing in most of the domestic journals through November 1949 and foreign journals through October 1949. It is more complete, however, than the previous one in that it includes physical as well as chemical testing methods. Like the previous one, it excludes test methods for the analysis of compounding ingredients and of raw materials used in the manufacture of synthetic rubbers. It does not in general refer to procedures which are more concerned with fundamental research problems than with testing methods. The review is also restricted to procedures which have already been applied to the analysis and testing of natural and synthetic rubbers, and not to general procedures of possible application in this field.

GENERAL

Besides the article previously mentioned (*27*) there have appeared within the past year several other review or summary papers. Brock, Swart, and Osberg (*48*) made an extensive coverage of the advances in the whole field of rubber technology for the years 1947 and 1948. Included in their review are references to papers dealing with testing methods. These same authors also published a similar article covering work through June 1949 (*47*). Paetsch (*174*) in Germany made a similar but much less extensive survey.

A series of six lectures sponsored by the Northern Polytechnic of London and delivered by senior members of the Research Association of British Rubber Manufacturers (*75, 141, 150, 155, 214, 253*) on various aspects of rubber testing is referred to in other portions of this paper. Duval (*78*) made a survey on standardization tests, and discussed the importance and advantages of international standard methods for testing and controlling the quality of latex, crude rubber, and finished rubber products. A survey was made by Lemée (*130*) of the more important physical and chemical tests on crude and vulcanized rubber currently used in the laboratory for controlling quality in production and for studying properties in research and development work. The report by a joint conference of the Association Française des Ingenieurs du Caoutchouc and the Institut Français du Caoutchouc (*17*) describes the test methods used for latex, raw rubber, compounded stocks, and vulcanized rubber. It also gives a short account of instruments used in recording and controlling some factory operations.

The various mechanical properties and testing of rubber were treated in lectures by Willis (*260*). Coinon (*65*) reviews the important physical tests performed on finished industrial rubber products, together with the equipment necessary to make these tests. Hammond (*97*) describes recent developments that point the way to quality products, and states that engineers are now demanding new information on rubber which cannot be obtained from the conventional tests. A bulletin prepared by Imperial Chemical Industries (*113*) describes and illustrates the facilities available at the laboratory at Blackley for the physical testing of rubber. As a supplement to a previous series of articles, Werkenthin (*251*) has started another series describing the more recent developments in the field of testing procedures used by the U. S. Bureau of Ships for the evaluation of natural and synthetic rubbers.

Several books published within the past year include information on the testing of rubber. Volume III of "Elastomers and Plastomers" (*111*), edited by Houwink, includes a chapter on chemical analysis by Epprecht (*79*), one on properties of elastomers by Boonstra (*35*), and one on methods of physical testing by Teeple (*228*). Chapter 2 of Burton's "Engineering with Rubber" (*55*) deals with the physical properties and testing of rubber. The Goodyear Tire and Rubber Company has recently published a book (*92*) which also approaches the subjects of properties and testing of rubber from an engineer's viewpoint. Rubber testing is included in a book printed in Dutch by Bokma and Kraay (*34*) on rubber and latex. Dawson, in his survey of "The Rubber Industry in Germany during the Period 1939–1945" (*73*), describes or refers to German methods of testing both synthetic latices and Buna rubbers. Treloar's new book, "The Physics of Rubber Elasticity" (*236*), presents no methods designed for testing but does include a description of general physical properties of rubbers such as elasticity, photoelasticity, crystallization, flow, stress, relaxation, and dynamic properties. The "Proceedings of the Second Rubber Technology Conference" (*74*), released in 1949, contains the papers that were presented at the conference held under the auspices of the Institution of the Rubber Industry in London on June 23 to 25, 1948. This book also includes an open discussion on the testing methods for tensile strength, hardness, abrasion, and tear testing on vulcanized rubber. This discussion reveals the chief differences in the methods as used by Britain, United States, France, Germany, and Italy in their standard procedures.

In the United States the American Society for Testing Materials has issued its annual compilation of standards for rubber (*4*), which contains revisions and additions to the previous edition. The Office of Rubber Reserve issued a revised edition of its "Specifications for Government Synthetic Rubbers" (*169*). This publication now appears in the form of a loose-leaf book to which changes or additions can easily be made from time to time. The U. S. federal specification (*242*) on methods of tests for rubber goods is in process of revision. The same is true for the methods for latex, crude rubber, and vulcanized rubber products, promulgated by the British Standards Institution (*46*).

Burk and Grummitt's "Recent Advances in Analytical Chemistry" (*53*) covers polarography, infrared spectroscopy, electron microscopy, and mass spectrometry, and presents a comprehensive picture of the current knowledge in each. This new book should be valuable to the rubber analyst in enabling him to understand and evaluate new techniques which may find application in rubber analysis or testing.

LATEX

The Rubber Research Institute of Malaya has issued instructions (*186*) in card form on the methods of sampling of preserved latex, determination of ammonia content, dry rubber content, and total solids of the latex. Boucher (*41*) has published a paper listing the various physical and chemical tests determined on latex for control testing in the laboratory, and describes measurements of viscosity, chemical and mechanical stability tests, and tests for tensile strength of the rubber obtained from casting or dipping the latex. Dawson (*72*) has described in considerable detail a rapid and simple mechanical stability test using high-speed stirring in which progressive flocculation of the latex continues until mechanical coagulation occurs. The colloid stability of the latex is defined as the time in seconds required to reach an arbitrarily defined end point. The author also reviews and discusses previous articles on mechanical, chemical, and heat tests of stability. Scott and Walker (*200*) found that changes in viscosity in the emulsion polymerization of chloroprene could easily be measured by the Mooney-Ewart rotating cylinder viscometer. Partridge and Hansen (*175*) described the drying of latex rubber deposits as taking place in two stages: the drying that brings about the coagulation of the rubber, and the evaporation of the remaining moisture from the film. The first step must be carefully controlled in order to prevent the formation of blisters.

The purchase of latex on the basis of specifications has rapidly become of increasing importance because a large number of new producers, particularly natives of the Far East, are entering the field of latex production and releasing a product of doubtful quality (*3*). The American Society for Testing Materials has therefore formed a subcommittee on latex which has drawn up a tentative set of specifications and tests for concentrated preserved latex (*5*). Specifications and tests of the latex include those on total solids (T.S.), dry rubber content (D.R.C.), alkalinity, viscosity, sludge content, coagulum content, KOH number, mechanical stability, copper content, manganese content, color on visual inspection, and odor after neutralization with boric acid.

UNVULCANIZED RUBBER

Purification. The preparation of highly purified samples is often important, so that properties and tests on these materials may be made without being influenced by the foreign substances. Verghese (*244*) describes a new method for the preparation of highly purified rubber hydrocarbon without resorting to any drastic chemical or mechanical treatments of the rubber. The proteins of the rubber latex are displaced by treating with ammonium oleate, with subsequent creaming. The same author (*245*) also fractionated his purified rubber and determined the molecular weights of each fraction. Martin (*145*) also mentioned the same procedure for the preparation of natural rubber to a purity of 99.9% hydrocarbon. MacLean, Morton, and Nicholls (*137*) described a procedure for the preparation of copolymers having a relatively narrow range of molecular weight and being relatively homogeneous as to comonomer composition on the chains.

Swelling. The swelling of natural and Buna latex films in water has been studied by Bächle (*18*). In the present procedures, immersion in water, the swelling is obscured by extraction which takes place at the same time. This extraction can be eliminated or greatly reduced by swelling in water vapor, or preferably by employing a "short swelling" technique—e.g., immersion for about 10 seconds. Furukawa and Iwasaki (*83*) studied swelling from a theoretical point of view and found a relationship between the swelling pressure and the increase in volume.

Refractive Index. Wood and Tilton (*263*) measured the refractive index of natural rubber for five different wave lengths of light in the visible region and at several temperatures. They made use of a spectrometer and observed the angle of minimum deviation produced by a prism of known angle. This method gives more precise results than the usual methods of critical angle refractometry.

Viscosity and Plasticity. In the past years the quality of different lots of natural rubbers has been judged to a considerable extent by tensile properties. Schidrowitz (*194*) reports that the most recently added test for quality is that of viscosity. This section of the paper deals only with the viscosity of the solid polymers and not of their solutions or suspensions. Reviews and discussions of the measurement of plasticity or viscosity using the various types of instruments have been made by Gauthier (*87*), Scott and Whorlow (*206*, *253*), and Legge and Einhorn (*129*). They seem to agree that each type measures a somewhat different property, but that they all have their places in control work. By means of the Goodrich plastometer, Furukawa and Tomihisa (*84*) studied the plasticity index of raw rubber, the effect of the magnitude of stress in the measurement of plasticity, and also the temperature coefficient of plasticity. Kilbourne (*118*) found that there was at present no single type of instrument for measurement of plasticity which supplies all the desired information for reclaimed rubber. The selection of a method depends on the type of processing in which the reclaim is to be used.

Whorlow (*254*) has investigated the efficiency of the Defo plastometer. In the article he gives a good description of the apparatus, including the test method, and some results of tests. His conclusion is that there is little to choose between the Williams and the much more elaborate Defo instruments for either experimental accuracy or for speed of test.

Treloar (*237*) studied the flow characteristics of natural and of GR-S rubbers over a range of temperatures using the Mooney viscometer modified with the biconical rotor of Piper and Scott. From the temperature coefficient of flow rate at constant stress he was able to calculate the activation energy for flow as about 10.2 kcal. per mole.

The R. T. Vanderbilt Company (*13*) describes in detail the method its laboratory uses for the operation of the Mooney viscometer, including scorch tests. Chalmers (*59*) also uses the Mooney apparatus and claims that the scorch test saves the rubber industry many dollars by indicating the conditions which produce scorched material. Somerville and Maassen (*12*, *215*) made test measurements at various temperatures from 220° to 280° F. and recommend operation at 250° F.

Molecular Weight and Structure. There have been many papers, both experimental and theoretical, published on molecular properties and structure. However, only a few of the experimental ones on the determination of molecular weight will be mentioned here, and the reader is referred to an extensive bibliography of this field, by Simha, Budge, Jeppson, and Callomon (*211*), which is now in preparation and will be published as a circular of the National Bureau of Standards.

Probably the most popular method of determining molecular weight of high polymers is by measuring intrinsic viscosities of their solutions. Scheele and Timm (*193*) give a review and survey of this method. Billmeyer (*30*) states that a good estimate of intrinsic viscosity can be obtained from one measurement of relative viscosity at a convenient concentration. Henderson and Legge (*104*) prepared their solutions by dissolving the butadiene-styrene polymers in toluene–isopropyl alcohol mixtures directly from the latex. Scott, Carter, and Magat (*207*) confirm a previous hypothesis that for essentially linear rubber polymers the intrinsic viscosity of the solution depends on approximately the two thirds power of the molecular weight. Johnson and Wolfangel (*116*) determined the relationships between the viscosity and the molecular weight for emulsion polybutadiene polymerized at three different temperatures. Relationships were also obtained for a Russian sodium-butadiene polymer (*266*), and for polyisobutylene by Fox and Flory (*82*).

Osmometric measurements for the determination of molecular weights are described by Zhukov, Poddubnyĭ, and Lebedev (*265*). Masson and Melville (*146*, *147*) describe a thermostated osmometer of the Fuoss-Mead pattern and the technique of preparing bacterial cellulose membranes. Henderson and Legge (*103*) developed an osmometer in which the nitrocellulose is deposited to any desired thickness on an alundum thimble. They show evidence that matched capillaries lead to erroneous results.

Brice (*44*) describes a photoelectric photometer which is designed for determining molecular weights of high polymers by measuring absolute turbidity, dissymmetry, and depolarization of dilute solutions of the materials. Hadow, Sheffer, and Hyde (*96*) describe a similar apparatus and discuss the degree and source of errors. Methods of calibration are also critically examined. Cashin and Debye (*57*) have made use of measurements of secondary absorption for this purpose.

Mark (*143*) in discussing the measurements of molecular sizes states that osmometry is best suited for materials whose molecular weights are between 20,000 and 600,000, and that light scattering serves well from 40,000 upward. Dogadkin, Soboleva, and Arkhangelskaya (*76*) obtained satisfactory agreement between the results of two methods for natural rubber and for butadiene-styrene polymers.

Other methods for determining molecular weights have also been used. Heller (*102*) makes use of dityndallism; Siegel, Johnson, and Mark (*210*) make measurements with the electron microscope; and Mochel and Peterson (*151*) determine end groups using radioactive sulfur. Garten and Becker (*86*) determined the size and shape of the Buna molecule by using viscometric and osmometric measurements, gelling, fractional precipitation, and oxidative scission. Munster (*157*) outlines the different physicomathematical concepts of thermodynamics and statistical mechanics of solutions of substances with high molecular weights.

Baker (*19*) studied a new macromolecule, which he calls microgel, and shows its relationship to sol and gel as structure elements of synthetic rubbers.

Flory, Rabjohn, and Schaffer (*81*) cross-linked natural rubber quantitatively to different degrees and determined tensile strengths on the vulcanizates. They found that a greater degree of cross linking produced vulcanizates having higher tensile strengths. Bardwell and Winkler (*20*) found that the tension exerted by stretching GR-S at a given temperature and elongation is determined by the initial molecular weight and the concentration of cross linkages.

CHEMICAL ANALYSIS

Solvent Extraction. The most commonly used procedure for the determination of the quantity of rubber in plants is that involving solvent extraction. Horel (*110*) applies the often-used differential extraction method in analysis of plants for resins and rubber. He uses a 12-hour extraction with acetone for the resins, followed by a 24-hour extraction with chloroform for the rubber. Metcalfe (*148*), in analyzing kok-saghyz roots, extracts the pulverized sample for 20 hours with acetone for the resins and 20 hours with benzene for the rubber. He adds a small quantity of phenyl-2-naphthylamine to the benzene extract to prevent oxidation.

Blow (*33*) describes a procedure for the estimation of small percentages of rubber in fibrous materials. Wool, leather, or silk is destroyed by treating with a boiling 5% solution of potassium or sodium hydroxide, after which the rubber is filtered or centrifuged. If cellulose fibers are present they are destroyed by boiling with concentrated hydrochloric acid, and the rubber is then dissolved in benzene and precipitated with acetone.

New aids have been suggested in apparatus design of extraction apparatus. Toeldte (*235*) illustrates a new condenser cooling system which eliminates dangers of flooding from condenser cooling water. Tryon (*240*) has a modified Soxhlet extractor which uses an unusually small amount of solvent even when employed as a large-scale unit. A simple conversion allows this extractor to be used under reduced pressure, and hence permits extractions at the lower temperatures necessary when working with materials unstable at the normal boiling point of the solvent.

Infrared. Mann (*142*) gives an extensive survey of the use of infrared spectroscopy in the chemical analysis of mixtures of elastomers and in the study of the structures of polymers. The application of this relatively new method to high polymers is described fully and many references are given. Saunders and Smith (*191*) have extended their previous work on the application of infrared spectra to study the structure of Hevea and gutta hydrocarbons. The absorption spectra of these two different classes of natural polyisoprenes, when determined on oriented crystalline films using polarized radiation, strongly confirm the accepted idea that the Hevea isomers are cis in configuration and that the guttas are trans. Treumann and Wall (*238*) have applied the infrared spectrometric method to the quantitative determination of the butadiene units which have undergone 1,2-addition in polymers and copolymers of butadiene. Hart and Meyer (*100*) show that the infrared spectrometer is not only valuable in determining the 1,2- addition but can also measure the trans-1,4 structure of these polymers. Hampton (*99*) extended the work still further and was able to determine the quantity of cis-1,4 addition and also the amount of combined styrene in GR-S synthetic rubbers. He was also able by means of the infrared to distinguish between the standard GR-S and the low-temperature–polymerized GR-S rubbers. King, Hainer, and McMahon (*119*) extended the infrared measurements on polymers to lower temperatures, even as low as those of liquid helium, but found no very significant changes in absorption. Young, Servais, Currie, and Hunter (*264*) and also Richards and Thompson (*183*) applied infrared studies to the silicones and related compounds and determined the characteristic bands for their structures.

Elemental. Madorsky and Wood (*138*), by careful and precise combustion analysis for carbon and hydrogen in butadiene-styrene copolymers, were able to compute the fraction of the hydrocarbon polymer which was derived from the styrene. Details of the analytical procedures are given, and the precision and accuracy of the measurements are discussed.

Proske (*180*) studied the determination of sulfur in rubber by means of the polarograph. He found that acetone as an operative solvent gave definitely low results, but that pyridine was satisfactory. Outa (*172*) determined the amount of sulfur in rubber after ignition of the sample in a bomb under a pressure of 40 atmospheres of oxygen. The sulfate is precipitated with benzidine hydrochloride and titrated with standard sodium hydroxide solution using phenolphthalein as indicator. Results agree within 0.2% of the calculated values. The procedure requires only about one hour for completion. Calcium and barium, however, interfere with the determination.

Van der Bie (*29*) studied the procedures for determining small quantities of nitrogen in crude rubber, trying the various modifications of the Kjeldahl method, including various catalysts, in an attempt to establish the best conditions with respect to speed, accuracy, and consistency. The resulting procedure is described in detail.

Chambers' method for the direct determination of oxygen by application of the Unterzaucher method, which was reviewed last year (*27*), has since been published (*60*).

Genova and Addobbati (*89*) contribute to the method of determining small amounts of copper in rubber by suggesting a new method for eliminating the interference of manganese. The slightly ammoniacal hot solution is treated with bromine water and then made alkaline with sodium hydroxide solution. Repeated treatments precipitate the manganese. Milliken (*149*) has been studying the question as to whether or not copper is lost during the dry-ashing process of preparing the sample for solution. It is concluded that with careful ashing over a short period of time and at temperatures not in excess of 550° C. there is practically no loss of copper. This ashing procedure is much simpler than the wet-oxidation method of solution of the sample.

Belmas (*28*), in his physicochemical studies of Hevea latex, has developed methods for the quantitative determination of the metals potassium, sodium, calcium, magnesium, and iron. He finds that both the dry method and the wet method for destroying the organic matter work very well.

Korshun and Sheveleva (*122*) have developed a polyelemental procedure for the simultaneous analysis of carbon, hydrogen, halogens, and sulfur in organic compounds. The sample is burned in an empty combustion tube in a stream of oxygen, and the exit gas passes over a silver ribbon which retains the halogens and sulfur. The usual water and carbon dioxide absorption tubes follow the one containing the silver.

Carbon Blacks. Paetsch (*173*) gave a review with discussion and references to methods for the analysis of carbon blacks, and also presented data on German carbon blacks. Bauminger and Poulton (*21*) also reviewed the more usual methods for estimating quantities of carbon black. They suggest a new procedure in which the rubber, either vulcanized or unvulcanized, is extracted with acetone, the volatile matter distilled off in an atmosphere of nitrogen, and the carbon in the residue then determined by loss of weight during combustion and also by absorption of the resulting carbon dioxide.

Kruse (*123*) describes a technique of determining particle size of carbon black in rubber by means of the optical microscope. The usual ultramicroscope formulas are used to calculate the average size of particles.

Brock (*49*) applies microradiography to rubber compounding problems. He has developed a technique which is valuable in determining the degree of dispersion of various pigments in elastomers. By this technique it is also possible to study the vacua which are formed around various pigment particles when a vulcanizate is elongated. This technique of microradiography is superior to that of microscopy for studying opaque rubber compounds.

Miscellaneous. Rush and Kilbank (*187*), in their study on the effect of moisture variation in the curing rate of GR-S, found that the hot-mill method for determining moisture is neither sufficiently sensitive nor absolute. They also found that heating methods sometimes volatilized some of the softeners. They therefore tried out and were able to apply successfully the Karl Fischer procedure, which they describe in their paper. Tryon (*239*) also ran into the same difficulties as Rush and Kilbank when applying the usual moisture methods to GR-S, but he elected to modify the azeotropic distillation method, using toluene and making it simpler and more precise by measuring the quantity of water in a calibrated capillary tube open at both ends. The inside of the apparatus is coated with silicone polymer to prevent water droplets from adhering to parts of the apparatus.

Budig (*51*) describes in detail the distinguishing characteristics and identification of some aging inhibitors by means of color reactions. These inhibitors include mercaptobenzimidazole, phenyl-2-naphthylamine (phenyl-β-napthylamine), and derivatives of phenylenediamine. Burmistrov (*54*) identifies diphenylguanidine, diazoaminobenzene, 1-naphthylaminoaldol, phenyl-2-naphthylamine, and tetramethylthiuram disulfide. Kul'berg and Blokh (*124*) developed spot tests for the identification of mercaptobenzothiazole, tetramethylthiuram disulfide, diphenylguanidine, diazoaminobenzene, and Aldol.

Madorsky, Straus, Thompson, and Williamson (*139*) pyrolyzed samples of polyisobutene, polyisoprene, polybutadiene, GR-S synthetic rubber, and polyethylene in a high vacuum (10^{-6} mm. of mercury) in a specially designed apparatus at temperatures ranging between 300° and 450° C. They found that upon analysis of certain fractions of the pyrolyzed products by means of the mass spectrometer each polymer gave a characteristic mass spectrum, and that pyrolytic fractionation therefore can serve as a means of identification of polymers. Wall (*247*) developed a mathematical relationship which gives the pyrolytic yield of monomers from copolymers. He substantiated this equation by mass spectrometric analysis on pyrolytic products of butadiene-styrene and of isoprene-styrene copolymers.

The only article that was found on the determination of the amount of unsaturation of butadiene rubbers by chemical methods during the year is an English translation (*243*) of a 1947 Russian article which was referred to in last year's review (*27*).

Moses and Rodde (*153*) developed a method for the testing of GR-S polymers for pigmenting, discoloring, and staining properties. They expose the polymer to ultraviolet radiation and note its tendency to stain lacquer. Pryer (*181*) studied the nature of ingredients used in rubber as related to their staining properties. Discoloration of a vulcanizate may actually take place from migration on rubbery surfaces when left in contact with other articles containing a staining ingredient.

Wisniewski (*261*) has observed and tested many samples of wild rubber from the Amazon Valley. From his experiences he states that even the expert rubber grader by his on-the-spot superficial examination is unable to detect many of the adulterants found in the wild smoked rubber balls. Chemical analysis, however, can easily detect them.

AGING

In March 1949 the American Society for Testing Materials held a symposium on aging of rubber under the chairmanship of Maassen (*135*). The first paper, by Neal and Vincent (*158*), discussed the mode of attack of oxygen on rubber, suggesting several possible chemical reactions in this complicated process. Shelton (*209*) reviewed the oxygen absorption methods of aging and presented their utility and limitations. Cole (*66*) discussed the chemical changes which take place during thermal or photochemical oxidation. Throdahl (*233*) described the physical aspects of aging of rubbers and the causes of their hardening or becoming tacky. Blake (*31*) told of the effects which light and ozone have on rubber. In the final paper of the symposium Schoch and Juve (*197*) discussed the effect of temperature on the air-aging of rubber vulcanizates.

Because of the slowness of the usual accelerated weathering tests for elastomers Phillips (*176*) devised a new and faster test in which both sides of a much thinner sample of rubber are exposed simultaneously to the sunlight. The softening and hardening of rubber with age and the role of oxygen in aging were studied by the London Advisory Committee for Rubber Research (*133*). Tew (*229*) summarizes the present knowledge of the resistance of natural and synthetic rubbers to ozone. Judeinstein (*117*) made a study of the increased tensile strength exhibited by rubber at the beginning of aging. His experiments included aging in the Geer oven, in oxygen, and in sealed vacuum tubes, and testing by the T-50 method.

The Research Association of British Rubber Manufacturers (*182*) has found that the material forming the mold surface for tensile specimens has an influence on the aging properties of the rubber vulcanized in the molds. Precise testing work must therefore specify the mold material and also the dusting agents or lubricants to be used. Throdahl (*234*) made a comparison between measurements of creep with some of the conventional aging tests and concluded that the chemical reactions caused by oxidation are fundamentally exhibited by creep and stress relaxation. Creep measurements can actually differentiate more clearly between the behavior of different antioxidants than the usual aging tests. Boonstra (*36*) measured the tensile properties of the vulcanizates of a number of different types of synthetic rubber at elevated temperatures. He prefers to call the tensile test at high temperatures the "heat resistance" test rather than "heat aging."

LeBras and Salvetti (*126*, *127*) made kinetic studies on the oxidation of rubber by a manometric method of oxygen absorption. These authors believe that this method can replace the oven or bomb tests for aging. They have also found (*128*) that mechanical stresses, whether static or dynamic, have no effect on the oxidizability of rubber. Stafford (*223*) describes an apparatus for measuring oxygen absorption of vulcanized rubber either in darkness or under illumination from a controlled light source. Pollack, McElwain, and Wagner (*179*) found sufficient correlation between the oxygen absorption rates and deterioration of physical properties on aging of rubber to justify the substitution of the oxygen absorption method for the longer standard procedures in evaluating aging characteristics of rubber stocks.

Sanders (*189*), in a study on the effect of light on neoprene, found that standard accelerated light-aging devices cannot always be used to predict the resistance of white GR-M vulcanizates to discoloration by sunlight. The artificial methods can, however, often be used for preliminary screening purposes.

Blake and Kitchin (*32*) studied the effect of microorganisms on rubber electrical insulation. Accelerated laboratory tests, using active fertile soil containing some moisture, having a pH of about 8, and maintaining temperatures from 70° to 95° F., developed in a few weeks or months failures which in actual underground service would require 10 years or more.

The British Ministry of Supply (*45*) has developed specifications defining test cycles of different temperatures, humidities, and pressures in attempts to simulate different climatic conditions. Rubber and other materials are subjected to these tests in studying resistance to fungus growth and other deteriorating influences. The R. T. Vanderbilt Company (*11*) studied the mildewing of rubbers in a mold cabinet and under soil burial. The conclusions from these tests were that all cured compounds are immune to attack by fungus, but of the raw rubbers only neoprene is immune.

MECHANICAL TESTS

Static Tension. A comparison of the tensile data obtained from Schopper ring and from Brittish standard dumbbell test pieces has been made by Scott (*203*) for a wide variety of rubber vulcanizates. Results show that the "true" value of the tensile strength, elongation at rupture, and elongation at a fixed stress deduced from data on rings agree on the average closely with the corresponding values obtained with dumbbell specimens.

Klute (*120*) believes that abnormally low values for elongation and tensile strengths are often obtained from dumbbell specimens because of uneven cutting edges in the dies. Careful honing of the inner die surfaces will help the situation. Higuchi, Leeper, and Davis (*105*) studied the effect of the size of the dumbbell specimens on the tensile strength of natural and GR-S synthetic rubbers and found that larger specimens give lower observed tensile strengths. Maron, Madow, and Trinastic (*144*) determined tensile strengths on samples of raw polymer films and gum vulcanizates prepared from GR-S latices. Results from the two types showed no correlation when the calculations were based on the original cross section, but when the results were based on the actual area at break the strengths of the raw polymer and the vulcanizates were found to be essentially the same.

By increasing the speed of jaw separation from 20 to 40 inches per minute in tensile testing one can increase the work output about 75%, without any appreciable change in the resulting data (*10*). Villars (*246*) went to very high speeds, up to 270% elongation per millisecond, which he found especially valuable for studying the stress-strain curves for crystallizable rubbers before crystallization had time to take place. A machine was developed by Chatten, Eller, and Gondek (*61*) for use in buffing strips of rubber materials such as hose, gaskets, etc., which require preparation before tensile testing.

Dahlquist, Hendricks, and Taylor (*71*) devised a constant stress method for elongation of soft polymeric materials. This they accomplished by means of a weight in the shape of a hyperboloid which is lowered into the water as the film stretches. The buoyancy reduces the load in proportion to the cross-sectional area of the test specimen.

Phillips and Labbe (*177*) developed an instrument which determines the rate of relaxation of elastomers under compression or shear as well as recovery after partial or complete release of load over a temperature range from −70° to +158° F. Macdonald and Ushakoff (*136*) describe a new compact instrument for measuring stress relaxation which contains a minimum of moving parts, is essentially free from draft and vibrational effects, and measures the relaxation characteristics of a substance under constant strain. Boonstra (*37*) uses a simple device for measuring the speed of retraction of rubber. He states that permanent set plays an important part in the complicated mechanism of retraction.

Jarrijon (*115*) made a special study of the variability in natural rubber from Indo-China, and suggests the determinations of mechanical properties of the vulcanizate as a means of estimating rate of cure, nitrogen content, and Mooney viscosity of the crude rubber.

Fletcher (*80*), in a preliminary investigation on the grading and testing of natural rubber, ruled out the tests on abrasion, flex cracking, and cut growth because of their inherent difficulties in measurement. He came to the same conclusion as Roth and Stiehler (*108*, *185*) that a more sensitive and reliable test is the determination of elongation of a rubber specimen subjected to a predetermined constant stress. He suggests the use of a vulcanizate somewhat different from that recommended by the Crude Rubber Committee of the Division of Rubber Chemistry, AMERICAN CHEMICAL SOCIETY, because of the great sensitivity of the latter formula to variations in moisture content.

Hardness. Späth has written several reviews and critical discussions on hardness, one on indentation hardness (*218*), another on Shore hardness (*219*) and a third on rebound hardness (*217*). Dubois (*77*) has made a study of the factors affecting hardness and recalls the different methods of measuring hardness, such as static, dynamic, and kinematic. Cooper (*70*) believes that tensile strength data are no longer adequate and are often impractical in evaluating the quality of a rubber compound, especially in control, and that hardness, modulus at chosen elongations, load deflection, and other characteristics are more important properties for evaluation of quality. In the paper the author discusses the merits of various hardness testers and their calibrations.

Scott (*201*) proposed to the British Standards Institution a new and improved method for expressing hardness of vulcanized rubber, the scale to read from 0 to 100 B.S. (British Standard) degrees, but to be in reverse order from the present British scale. The 0 reading is for an infinitely soft, and the 100 for an infinitely hard material. Over most of the scale the readings are practically identical with the Shore Durometer A readings. Soden (*214*) gave a survey of hardness tests and described the new proposal of Scott's. Hammond (*97*) reviews the field of hardness testing and also recommends the adoption of the newly proposed scale in England. In a later article Scott (*202*) reported that the new scale had met with no adverse comments and would therefore be accepted as standard. Newton (*161*) made a thorough study of the accuracies of hardness testing for the different types of gages used, and described the errors associated with each type.

Abrasion. Scott, Newton, and Willott have written four more of a series of articles on the determination of resistance to abrasion. In the first (*204*) it was concluded that rubber compounds of the tire-tread type are not appreciably influenced by the direction of the grain in the compound, which in a tire runs around the periphery. The second (*162*) shows that marked deterioration takes place with all types of abrasive wheels with use, and that attention must therefore be paid to the statistical planning of tests so that these factors can be reduced or eliminated. In another investigation (*163*) they found that the use of an abrasive index (abrasive resistance relative to a standard rubber) for expressing test results does not enable different types of abrasives to be used indiscriminately because different abrasives sometimes give widely different indexes for the same rubber. The fourth article (*205*) gives a comparison of the Akron and the Du Pont abrasion machines, and concludes that they do not give the same abrasive index for the same rubber. In general, however, a factor can convert the value obtained from one machine to that of the other.

Griffith, Storey, Barkley, and McGilvray (*95*) could not find agreement between laboratory abrasion tests and service performance of a recapping compound. They attribute this to the formation of a viscous film on the abrasive and on the surface of the abraded rubber, which lubricates the abrasive and gives an abnormally low loss. When, however, the rubber is extracted with ethyl alcohol–toluene azeotrope, there is no film and good correlation is found between the laboratory and the road tests. Späth (*216*) discusses the question of wear in pneumatic tires and its relation to tire temperature and speed of travel.

Adhesion. A series of papers has been written by Hammond and Moakes (*98*) and by Borroff and Wake (*38*, *39*, *40*) on the adhesion of rubber to textiles. They describe the testing technique and also the factors influencing the load requirements to strip rubber from fabric and foil surfaces. Pittman and Thornley (*178*) developed a dynamic test for the measurement of the adhesive forces between rubber and cord fabric. The test piece consists of a single cord surrounded by a thin cylindrical layer of casing compound which is enclosed and protected by a thicker layer of rubber of standard composition. The test pieces are subjected to controlled bending and compression. Gardner and Williams (*85*) used destruction in shear to test the strength of bonds between rubber and cord. The test specimens were subjected to alternating compression and release in a Goodrich flexometer.

Anderson (*6*) describes and illustrates an instrument which records the force required to separate two layers of pliable materials cemented together. Results show a linear relationship between the peeling force and the logarithm of the peeling velocity. Moses and Witt (*154*) use ultrasonic vibrations in a direct quantitative method for measuring adhesion of organic coatings to either metal or nonmetal substrata. Werkenthin (*251*) describes the tests used by the U. S. Bureau of Ships for the measurement of adhesion.

In a study of rubber-rayon adhesion Thoman and Gilman (*231*) concluded that the strip test of the American Society for Testing Materials, which peels a woven fabric from a rubber-fabric sandwich, is more useful for general development work than the H-test, which pulls a single cord out of a block of rubber.

Lambert and McDonald (*125*) designed a new tackiness meter which reduces manual operations to a minimum. The machine measures the force required to separate sheets of rubber which have been pressed into contact. Schmidt (*196*) also built a new apparatus for the measurement of tackiness. The rubber is first calendered onto fine cotton fabric; part of the material is made into a disk and another part is placed around a pendulum hammer. The apparatus indicates the tackiness by means of measurements of rebound and the number of pendulum beats. Beaven, Croft-White, Garner, and Rooney (*23*) developed a quantitative tackiness meter which can use either short-period loadings or long-period loadings of the contacting rubber surfaces. Beckwith, Welch, Nelson, Chaney, and McCracken (*24*) modified the procedure of Busse so that they could measure the tackiness of fresh-cut surfaces of Butyl rubber.

Dynamic. Braendle, Steffen, and Dewender (*42*) state that many of the most commonly performed laboratory tests on rubber do not give a proper forecast of the usefulness in rubber, and that the trend during the past few years has been more toward the dynamic form of test. It is probable that development of future tests will start in the mill room. Mullins (*155*) gives a review of the recent developments in dynamic properties. Nolle (*165*) describes several methods for measuring the complex dynamic Young's modulus of rubberlike materials under conditions of small sinusoidal strain variations at various frequencies and temperatures. This paper by Nolle later was the subject of comments by Hillier, Kolsky, and Lewis (*107*) and also by the author himself (*166*). Chilton (*62*) discussed the application of large deformation stresses to elastic solids, and laid special emphasis on shear and torsion analysis because of their importance to practical applications.

Buchdahl, Nielsen, and Revreault (*50*) describe measurements for dynamic elastic modulus and mechanical dissipation factor for a series of high polymers as a function of temperature. Data were obtained by three different methods: electromagnetic vibrations, torsion pendulum, and rotating cantilever beams. Catton, Krismann, and Keen (*58*) determined the dynamic characteristics of neoprene vulcanizates from measurements made on the Du Pont-Yerzley oscillograph for mechanical properties and the Goodrich flexometer for the heat build-up.

Smith, Ferry, and Schremp (*213*) made measurements on the mechanical properties of polymer solutions. The concentrated solution of polymer is sheared by a rod oscillating axially with a very small amplitude, and the dynamic rigidity and viscosity of the solution are calculated from the measured mechanical impedance. Ashworth and Ferry (*16*) determined the rigidity of solutions of polyisobutylene from studying the propagation of transverse waves in several solvents as a function of frequency, temperature, and concentration.

Nolle and Mowry (*167*) made measurements on the velocity and attenuation of bulk waves in solid samples of high polymers by an acoustic pulse technique. The velocity was found from the change in echo arrival time when a sample is introduced into the sound path, and the attenuation was found from the reduction in echo intensity. Ivey, Mrowca, and Guth (*114*) also studied the propagation of supersonic waves in bulk rubbers. Sack and Aldrich (*188*) studied the elastic losses at ultrasonic frequencies of elastomer sheets of different thicknesses.

Hillier and Kolsky (*106*) developed a method for the investigation of the transmission of sound along filaments of high polymers. Tests were made of dynamic elasticity and damping factors of filaments when unrestrained and when being elongated at a constant rate of increase of strain. Witte, Mrowca, and Guth (*262*) made measurements of velocity and attenuation of audiofrequency sound waves in thin strips of GR-I and GR-S gum stocks in order to obtain their dynamic viscoelastic constants.

Shaw (*208*) gives a survey of the methods and machines used in the measurement of resilience and classifies them as to types. Clouaire (*63*) made a systematic study of stress-strain curves for pure-gum natural rubber by means of a dynamometer for the purpose of examining hysteresis phenomena in rubber undergoing cyclic strains of very low frequency. For slow deformations and large amplitude the author states that crystallization is the most important factor, but for rapid deformations of small amplitude (vibration) the loss of energy results chiefly from internal friction (*64*). Späth (*220*) presents some critical comments on the testing methods for impact resilience. He includes elastic modulus effect, dependence of impact energy, and the relation between resilience and hardness by indentation.

Oberto and Palandri (*168*) describe two new methods of test for the evaluation of energy losses due to hysteresis. The samples are deformed, respectively, in shear and in tension. Mooney and Black (*152*) developed a hysteresis test which measures directly the energy loss per cycle of elongation. The force is measured continuously while the machine is in operation. Storey (*227*) gives an evaluation of the flex-life and heat build-up properties in the elastomers. A linear relationship was established between the state of cure, as measured by dynamic compression of the vulcanizates, and the flex-life and heat build-up properties of the vulcanizate.

Wilkinson and Gehman (*259*) made hysteresis measurements with the Goodyear-Roelig machine, in which the test piece, under compression loading, is oscillated mechanically by a continuously adjustable eccentric weight rotated by a variable-speed motor. The hysteresis loop is traced by a beam of light from a system of optical levers attached to a dynamometer. The machine was found to be very versatile, and was compared with the Goodyear vibrotester, rebound pendulum, and flexometers.

Upham (*241*) compared resilience with abrasion resistance for vulcanizates of rubber, and came to the conclusion that one property could not be predicted from measurements of the other.

Miscellaneous. Mullins (*156*) says that "permanent" set of a loaded vulcanized rubber is almost entirely due to the way in which the filler particles are rearranged by stretching and is largely recoverable. It is therefore not a true property of the rubber molecule. Gavan, Schneider, and Abbott (*88*) improved a testing jig for a compression set determination of the American Society for Testing Materials (D-395, Method B).

A description of the method of tear test now used at the Rubber Research Institute T.N.O. at Delft, Holland, has been given by Nijveld (*164*), who thinks this method should be preferred over all others. Buist (*52*) studied both tear initiation and tear propagation. They are both important and determined by different types of tear instruments, and the methods for determining each should not be considered as alternative. Newman and Taylor (*159*) developed a microscopical method for the determination of the profile of the edge of rubber test specimens cut with a die. The condition of the edge of the specimen is of very great importance in certain tests, such as tear resistance.

Thirion (*230*) describes a device for the testing of the frictional properties of rubber. He gives the effects of pressure and contact area, sliding speed, temperature, surface moisture, tracks, and the conditions of the surface.

Conant, Dum, and Cox (*67*) describe and illustrate a laboratory apparatus, technique, and measurements of the coefficients of dynamic and static friction of tread-type compounds on ice. Their method is claimed to be capable of indicating with a fair degree of accuracy the tractive ability of a tire-tread compound on ice in actual service.

Conant, Hall, and Thurman (*68*) describe the methods they used for studying the relationship between the Gough-Joule coefficients and the moduli of vulcanized rubbers of different types.

ELECTRICAL TESTS

Livingston and Porteous (*132*) give a survey of the methods for finding the dielectric power factor of an insulator. They then describe two new methods which may be applied either in the field or in the works laboratory for the testing of high-voltage insulation. Whitehead and Rueggeberg (*252*) present a method for the measurement of dielectric loss at high frequencies and under changing temperatures. Alpers and Gast (*2*) developed a new method for determining the dielectric constant of materials in the form of small balls suspended on a torsion balance in an electrostatic field of varying frequency and varying temperature. Schallamach and Thirion (*192*) applied measurements of dielectric loss to swollen rubbers from −180° to +70° C. and over a wide range of frequency and found that polar swelling agents caused maxima at two different temperatures.

Scott (*199*) found directional effects in dielectric properties of molded rubbers. He prepared his samples in such a way as to accentuate greatly the flow in a given direction during sheeting and molding. For some mixtures the dielectric values were much higher in one direction than in the others. Holzapfel (*109*) describes methods which he used in determining the dielectric constant, loss factor, and breakdown strength of silicone rubbers.

Roelig and Heidemann (*184*) found a close parallel between the elastic and the dielectric properties of Buna polymers. They are able to estimate the styrene content of a butadiene-styrene polymer system by determining the temperature of maximum loss angle. Späth (*221*) also studied dielectric properties of natural and synthetic rubbers along with rebound tests over a wide range of temperature.

TESTS AT LOW TEMPERATURES

An improved low-temperature brittleness test has been developed by Smith and Dienes (*212*). The apparatus is capable of handling five specimens simultaneously and can operate as low as −130° C. Another new brittleness tester made by Scott Testers, Inc. (*9*), features small size and low weight for reasons of easy portability. In studying stiffness as applied to rubber, Stechert

(*224*) came to the conclusion that a fundamental measure of elasticity cannot be obtained in a practical manner by use of the A.S.T.M. tentative method test for stiffness in flexure on nonrigid plastics (D 747–43T). He therefore is attempting to develop a new bending test and claims encouraging results.

Because stiffening in rubberlike materials is probably caused either by actual crystallization of the molecules or by a second-order transition, measurements of the temperatures of these transitions are becoming more popular. The National Bureau of Standards has continually been improving the technique of volume dilatometry and has recently applied it to the determination of these transition temperatures for rubbers (*26*). Lucas, Johnson, Wakefield, and Johnson (*134*) studied molecular regularity in polymers by this method of volume measurement. Kolb and Izard (*121*) used a density balance to study transitions in higher polymers. Weir, Leser, and Wood (*250*) studied the same effects in silicone rubbers by means of the interferometer. Wiley and Brauer (*43, 255–258*) determined the temperatures of second-order transitions by making measurements of the refractive indexes over a range of temperatures by means of a refractometer to which they adapted a low-temperature bath capable of reaching −120° C.

Goppel and Arlman (*14, 15, 93, 94*) used an x-ray technique to measure the degree of crystallization in natural rubber. Stein, Krimm, and Tobolsky (*225*) found that by measuring birefringence of polymeric materials at different temperatures they noticed configurational changes in the region of the second-order transition.

Springer (*222*) prepared a survey article on physical properties of natural and synthetic rubbers and their relation to structure, especially as to the brittle point. At this temperature anomalies occur in curves for volume, dielectric constant, rebound, specific heat, and elastic modulus. Buchdahl, Nielsen, and Revreault (*50*) studied the transitions of some high polymeric materials from changes in dynamic modulus and dissipation factor. Schulz and Mehnert (*198*) describe a method for obtaining tensile strengths of rubbers at low temperatures, which gives information on the brittle points of the materials.

TESTS ON SPECIFIC PRODUCTS

The Adamson United Company (*1*) describes a "landing strip" for aircraft tire testing which is a flywheel having peripheral speeds up to 250 miles per hour. This testing unit was prepared for the use of the U. S. Air Forces. A British publication gives details regarding an x-ray apparatus (*7*) for the detection of cavities, cracks, and other flaws in tires.

The physical evaluation of foamed latex sponge was the object of study by Conant and Wohler (*69*). They described methods for determining tensile strength, compression modulus, and fatigue resistance, and the use of the results of these tests in determining quality and comfort.

Beatty and Cornell (*22*) describe the laboratory testing of rubber bearings. Smaller models are usually built for preliminary testing, but the final conclusions are always based on proving tests performed on a full-scale machine.

Hurry and Chalmers (*112*) applied photoelastic tests to rubber technology, and showed that it is a practical and reliable method for use in designing rubber products. The apparatus is inexpensive and the technique is simple.

FACTORY CONTROL

Control of processes in the factory is becoming more automatic. Oladko (*171*) has developed a calendergraph for the quality control of finished products. It provides a chart with which to guide the calendering processes. By means of gage measurements and automatic control of extruders Sanford (*190*) has been able to improve the uniformity of rubber covering of wire. An electrical control determines the speed with which the wire feeds through the extruder. Diagrams and descriptions (*8*) are given of electrical drives and electronic controls which regulate speed, roll adjustment, and other conditions. Walter (*249*) describes instruments in current use for the measurement of dimensions, weight, time, temperature, flow, volume, hygrometer conditions, and pH. Stolz (*226*) also describes the use and development of electronics in the rubber industry. Carlin (*56*) applies beta-ray backscattering to industrial gaging by means of equipment which consists of a radioactive source and a radiation detector. The degree of absorption or attenuation of the radiation of the material, which passes between these two parts of the instrument, serves as a measure of the weight per unit area or the thickness of the material.

Oladko (*170*) has applied control-chart technique of statistical control of quality to the plasticity of rubber mixtures during processing. Gnaedinger (*90, 91*) analyzes chart-control data by statistical methods to show the dependence of viscosity on various factors and the correlation between testing during processing and the testing of final quality.

Schmalz (*195*) discusses statistical techniques in the rubber industry. Control charts gather data for study, analyze special data, and help to establish specifications. From them is obtained the maximum amount of reliable useful information relating to the influence of variable factors on processes or products at a minimum of expense.

By means of a new meter Havenhill, Carlson, and Rankin (*101*) measured the electrostatic field strength and polarity of the charges produced during mastication of natural rubber and of GR-S. The apparatus shows promise as a new tool not only for process control but also for fundamental investigations on mastication, pigment dispersion, and even on concepts concerning the structure of matter.

Behre (*25*), in developing a new method for the determination of the activity of rubber fillers, found a rough parallelism between power consumption and the surface area (or activity) of the fillers.

Walter (*248*) describes and illustrates by means of photographs three new laboratory instruments for the rubber industry. The first is a combination mixer-calender, which can be used as a mixer with the cylinders on the same level, or as a calender with the cylinders shifted to one above the other. The second is a laboratory autoclave used for testing polymerization reactions or curing rubber mixtures. The third is a universal laboratory table containing a majority of the instruments used in a rubber laboratory. All these instruments are driven by a single motor.

STATISTICAL METHODS

Thornley (*232*) discusses various ways in which modern statistical methods may be employed to deal with typical problems in the rubber industry. Reference is made to the use of these methods for investigating the general accuracy of the various testing procedures. Mandel (*140*) wrote a paper on statistical methods in analytical chemistry in which he used as examples data obtained on water absorption tests on synthetic rubber and on the ultraviolet absorption of GR-S in methyl cyclohexane. Modern statistical methods have also been applied by Linnig, Mandel, and Peterson (*131*) to the design and interpretation of results in a study of a new complete-solution procedure for the determination of fatty acid, soap, and stabilizer in GR-S. Statistical methods in scientific experiments actually do not require vast amounts of data if the experiments are designed properly.

Newton (*160*) has presented a paper on the meaning of test results. Laboratory tests should be improved so that their results correlate with those obtained in service, and also so that interlaboratory variation is reduced. The subject of errors is discussed.

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WATER ANALYSIS

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THIS is the second review of analytical methods that have been applied to the analysis of water and reported in the technical literature. The first review (*56*) covered a 5-year period that extended through the early fall of 1948. The present paper covers methods published during the past year. Some of the original papers to which references are made were published earlier than the closing date of the first review but did not appear in abstract form, which is the source of much of the material in this report, until late 1948 or 1949.

In water chemistry, as well as in other branches of chemistry, analytical chemists are coming to rely more and more on instrumentation. Not only do modern laboratory instruments speed up the production of the chemist, but in many determinations they increase the precision and accuracy of the results. This is especially true of the various forms of photometers in the field of colorimetry. A word of caution, however, is offered for inexperienced analysts. The instrument has never been made that can be placed in operation and presumed to function indefinitely without attention. By their very nature most analytical instruments are extremely sensitive and require careful adjustment and frequent checking. The tendency of the inexperienced analyst is to trust implicitly the results obtained from a good-looking instrument. In fact, the more impressive its appearance, the greater the tendency to accept the results without question. With proper care, however, and frequent calibration or checking against known standards, modern laboratory instruments can lead to increased production and greater reliability of the results obtained by the water analyst.

SILICA

Very little was reported in the literature during the past year about the determination of silica in water. An analytical colorimetric micromethod was described by Verbestel, Springuel, and Royer (*103*) using ammonium molybdate. An accuracy of 0.05 mg. per liter, ±10%, is claimed.

Silica in sea water is assumed to be present as silicate, according to Robinson and Thompson (*81*). The silicate is determined colorimetrically with ammonium molybdate. Standards are prepared from solutions of potassium chromate, buffered with borax, or picric acid.

ALUMINUM, IRON, AND MANGANESE

The indirect method for the determination of aluminum by difference in the R_2O_3 precipitate ordinarily is not satisfactory for water analysis. Several direct methods have been developed using organic reagents, but in most of them iron or other cations interfere. Davenport (*20*) used 8-hydroxy-7-iodo-5-quinolinesulfonic acid (ferron) which forms a complex with aluminum when buffered with acetate–acetic acid solution to pH 5. The solution obeys Beer's law for concentrations of 0 to 40 micrograms of aluminum in 25 ml. Iron interferes but may be accurately determined by spectrophotometric measurement of the same solution at another wave length. A method for the direct precipitation of aluminum in the presence of iron, reported by Wilson (*109*), may be applicable for water.

The determination of iron in colored waters has often been unsatisfactory owing to the formation of complex ions with humic acids. Bezel (*10*) reported that iron can be released from the complex ion by baking the residue remaining on evaporation to remove the humates, and then determined in the usual way after dissolving in hydrochloric acid and oxidizing with hydrogen peroxide. Kaufmann (*43*) pointed out that such substances as hydrogen sulfide, thiosulfate, colloidal sulfur, cyanide, ferro compounds, cystine, and glutathion, even when present in small quantities, retard the oxidation of ferrous to ferric iron. Sulfite tends to accelerate the oxidation, while sulfanilamide, sulfathiazole, and sulfate have no effect.

Small quantities of manganese in water were determined colorimetrically by Gad and Priegnitz (*28*) using the Volhard method. The manganese is oxidized to manganese dioxide by lead dioxide and adsorbed on the lead dioxide. The residue is treated with hot nitric acid, presumably to convert to permanganic acid which is compared with potassium permanganate standards. As little as 0.1 mg. of manganese per liter can be determined by this method.

Harvey (*34*) used the periodate method to determine manganese in both fresh and salt water but developed a blue color by using tetramethyldiaminodiphenylmethane (tetrabase) in acetone.

CALCIUM AND MAGNESIUM

When calcium is separated from magnesium by precipitation as calcium oxalate, the coprecipitation of a small amount of magnesium is unavoidable. Studies made by Shvedov (*90*) using a radioactive indicator show that coprecipitation can be reduced by control of temperature of solution, speed of neutralizing, and rate of stirring. The rapid determination of small quantities of calcium using picrolonic acid or its lithium salt with methylene blue was described by Klement (*47*).

Abrahamczik (*3*) and Pieters (*75*) reported the successful use of Titan yellow for the colorimetric determination of magnesium. Taras (*97*) used Brilliant yellow for magnesium, but found that zinc and manganese must be removed.

HARDNESS

A method for the direct titration of hardness came into prominence during the year that appears destined to replace the long-familiar but seldom-precise soap method. Strangely enough, very little information has been published on the subject. The method is based on the work of Schwarzenbach and Ackerman (*87*) and Biedermann and Schwarzenbach (*11*). Betz and Noll (*9*) have published a summary of the method which tells where more detailed information may be obtained.

The new titration method for hardness depends on the ability of the sodium salt of ethylenediamine tetraacetate to sequester calcium and magnesium quantitatively. Several dyes have been used to detect the end point. Accuracies approaching those normally expected of quantitative methods for calcium and magnesium have been reported.

The use of potassium oleate to determine hardness was reported by Bukina and Govorova (*17*) to compare favorably with the palmitate method. Lopez *et al.* (*54*) used the palmitate procedure but added kaolin or talc during the standardization of the palmitate solution to produce the characteristic cloudy appearance similar to that caused by hardness in natural waters.

The Clark procedure for hardness underwent further revisions. Janssen and Spruit (*41, 42*) made turbidimetric and nephelometric studies of the method for waters of very low hardness using both potassium and sodium oleates.

According to Ozhiganov (*66*), hardness values can be determined with an accuracy of 1 to 3% by using a volumetric sodium phosphate procedure. A review of methods for determining hardness of boiler waters was presented by Pieters (*74*) in which the stearate method of Blacher–Van der Meulen was recommended. Sokolov and Komarova (*93*) described the tropeolin procedure utilizing a standardized colorimetric scale. Procedures for rapid determination of hardness using ion exchange materials were described by Bergman (*8*) and Blumer (*15*).

COPPER, LEAD, AND ZINC

The spectrophotometric determination of copper was reported by West and Compere (*108*) using malonic acid, gum arabic, and dithio-oxamide. The malonic acid prevents interference by iron.

The microdetermination of lead by chromatographic analysis was described by Lecoq (*52*). The lead is first absorbed in a column of alumina and the color is subsequently developed by addition of a 1% solution of sodium sulfide. A micromethod developed by Snyder, Barnes, and Tokos (*92*) for determining lead in air is also applicable to water. In the procedure for water the sample is treated with iodine solution and a solution containing potassium cyanide, sodium sulfite, and sodium citrate. The lead is removed with dithizone and compared with permanent color standards.

Gad and Naumann (*27*) found that the presence of small amounts of silver in water sterilized with silver ions interferes with the Winkler test for lead. Lead is separated from silver, and from copper when present, by precipitation with a suspension of calcium carbonate in the presence of potassium cyanide. The lead is redissolved in acetic acid, treated with 10% sodium sulfide, and compared with standards.

The use of the dithizone colorimetric method for zinc was reported by Corson (*19*) as being applicable for the routine checking for zinc in plating wastes that find their way into streams. The author described a simple control procedure in which all samples are compared with a 3 p.p.m. standard, and a detailed analysis procedure for determining from 0.0 to 8 p.p.m. of zinc.

SODIUM AND POTASSIUM

The use of the flame photometer for the determination of sodium and potassium in water appears to be increasing. Some of the earlier difficulties resulting from poor mechanical or optical design have been largely eliminated. A reduction in the errors in flame photometry was discussed by Bills *et al.* (*13*) and by Parks, Johnson, and Lykken (*68*). The use of suitable interference filters and acetylene or illuminating gas was described by Riehm (*78*). The amounts of sodium and potassium present in 150 public water supplies were determined with the flame photometer by Bills *et al.* (*14*).

Borgioli and Iacozzilli (*16*) determined sodium both titrimetrically and colorimetrically by using either uranyl zinc acetate or uranyl nickel acetate. Potassium was determined gravimetrically by using a 10% solution of sodium 2-chloro-3-nitrotoluene-5-sulfonate reagent.

ALKALINITY AND CARBON DIOXIDE

New indicators are still being tried for determining alkalinity. Taras (*98*) described another dye of the diazostilbeneaminedisulfonate series (Hessian Bordeaux) which in acetone solution gives a sharp pink to blue color change at pH 8.2. Free chlorine, which destroys the indicator, can be removed with sodium thiosulfate. A potentiometric method for determining the alkalinity of soft waters was described by Pekkarinen (*72*) using two samples of water that are brought into equilibrium with air containing different but known pressures of carbon dioxide. A similar procedure was reported by Kauko and Komulainen (*44*).

A method for determining the concentration of carbon dioxide by establishing equilibrium between the sample and the carbon dioxide content of saturated air was reported by Pekkarinen (*70*). The theoretical relationships governing the concentration of carbon dioxide in water as a function of pH and alkalinity were discussed by Schmassmann (*86*). Similar studies including graphic solutions of carbon dioxide–carbonate equilibria were made by Hallopeau (*32*).

pH AND ACIDITY

Difficulty in obtaining constant pH readings in water samples containing carbon dioxide was reported by Pekkarinen (*71*). Air containing carbon dioxide equal to the amount in the sample is bubbled through the sample during the pH measurement to obtain constant readings. An application of the colorimetric determination of pH to high-pressure well head water (up to 2500 pounds per square inch) was described by Shock (*89*).

The determination of pH and acidity of mine waters in the anthracite coal fields of Pennsylvania was described by Felegy, Johnson, and Westfield (*25*). For free acidity the sample is treated with 10% potassium iodide to reduce ferric to ferrous iron and thus prevent hydrolysis and liberation of sulfuric acid. Enough sodium thiosulfate is added to decolorize any liberated iodine, and the sample is titrated at room temperature to the methyl red end point. For total acidity the sample is boiled 3 minutes and titrated hot to the first permanent pink color of phenolphthalein.

SULFATE

Very little has been published during the past year on the determination of sulfate in water. De Salas and Valle (*22*) employed sodium rhodizonate in the volumetric titration of sulfate using 0.025 *N* barium chloride in solutions containing 25 ml. of sample and 25 ml. of ethyl alcohol. The authors claim no interference by ordinary concentrations of iron, aluminum, calcium, magnesium, sodium, potassium, chlorine, or nitrate.

Wenger, Monnier, and Hoffmann (*106*) reported that the mercuric nitrate method is satisfactory for the semiquantitative determination of sulfate in mineral waters.

CHLORIDE

Although potassium chromate has been successfully used for many years as an indicator in the argentometric titration of chloride, new indicators are constantly being tried. Hirano (*37*) used a test paper impregnated with *p*-dimethylaminobenzylidenerhodanine as an external indicator for determining small quantities of chloride. Mehrotra, Tewari, and Dube (*59*) reported a sharp reversible end point in dilute solution with no coagulation of precipitate by using resorcinol-succinein (succinyl-fluorescein). Bijker (*12*) determined the chloride content of river water by means of a recording conductivity meter. Presumably the ratio of chloride to total dissolved ions in the water was sufficiently constant to relate chloride to conductance readings.

FLUORIDE

The Scott-Sanchis procedure for fluoride was modified by Stevens (*96*) by substituting thorium for zirconium. In the Stevens modification the sample is buffered to pH 2.8 or 3.3 and then titrated with standard solution of thorium nitrate. Sulfate interferes but can be compensated by adding sodium sulfate to the standards. Milton (*61*) found that the dye chrome azurol S can be substituted for the alizarin indicator commonly used for fluoride.

A micromethod for fluoride was described by Stetter (*95*), which is based on the action of fluoride ions on potato phosphatases. At pH 3.8 the test is reported sensitive to 0.02 microgram per ml., and quantitative determinations are possible in the range 0.05 to 1.0 microgram with an accuracy of ±0.001 to 0.01 microgram, depending on the range of the standard curve.

NITRATE AND NITRITE

The diphenylamine reaction used in the determination of nitrates in water was studied by Lopez and Fungairiño (*55*). They reported being able to determine as low as 0.1 p.p.m. of nitrate. A sensitive reagent for determining nitrate in sea water was reported by Rochford (*82*). The author gives directions for preparing Harvey's reduced strychnine reagent for this purpose.

Leithe (*53*) described a method for the microchemical determination of nitrate in the presence of nitrite in water and soil extracts. An accuracy of 0.004 mg. of nitrate is claimed. The colorimetric determination of nitrites in sea water was reported by Robinson and Thompson (*80*) using α-naphthylaminesulfanilic acid. A specific reagent for nitrites was used by Pfeiffer (*73*). This reagent, *o*-aminobenzalphenylhydrazone, gives a violet-red color with nitrites owing to diazotization.

PHOSPHATE

Phosphate in water is almost always determined by utilizing the molybdenum blue reaction. A great variety of modifications have been employed to produce desired results under different conditions. The molybdenum blue reaction was studied by Clausen and Shroyer (*18*) with special reference to characteristics of the blue spectra between 400 and 800 mμ.

Baker (*5*) determined phosphate in boiler water by use of molybdic acid and 1-amino-2-naphthol-4-sulfonic acid solution dissolved in sodium sulfite and sodium bisulfite solutions. The blue color was read in an electrophotometer. The effective range is reported to be 10 to 100 p.p.m. of phosphorus pentoxide.

Phosphate in sea water was determined colorimetrically by Robinson and Thompson (*79*) by reduction of phosphomolybdic acid complex with stannous chloride. It was necessary to control concentration of chloride in the standard solutions. Harvey (*33*) determined phosphate as well as total phosphorus in sea water by means of the molybdenum blue reaction.

The amount of phosphate present in cooling water was determined by Rudy and Müller (*84*) by application of the Boratynski-Glixelli method to water treated with sodium hexametaphosphate. The authors state that orthophosphate can be determined in the presence of metaphosphate.

CHLORINE, CHLORAMINE, AND CHLORINE DIOXIDE

Artificial color standards for use in the determination of free chlorine in water, which are claimed to be reliable for 3 to 6 months, were made by Dubrovskiĭ (*23*). They are made by making mixtures of varying amounts of methylene blue, fuchsin, potassium chromium sulfate, and hydrochloric acid. Golubev (*29*) found that a color density proportional to chlorine concentration could be obtained by use of the reagent tris-(*p*-dimethylaminophenyl) methane-trihydrochloride (crystal violet). The color ranges from weak violet to deep violet corresponding to 0.1 and 0.6 p.p.m. of chlorine, respectively.

Palin (*67*) described a titration procedure to determine chlorine and the chloramines. A mixture of sodium hexametaphosphate and neutral *o*-tolidine in 100 ml. of sample is titrated with a ferrous solution until the blue color is discharged. This end point represents the free chlorine and two thirds of the trichloramine if present. Potassium iodide is added and the titration continued for monochloramine, and then dilute sulfuric acid and sodium bicarbonate are added and the titration is continued for dichloramine. Trichloramine is determined on a separate sample by extraction with chloroform and subtracting from the reading for free chlorine.

The determination of chlorine dioxide and other chlorine compounds by means of amperometric titrations was described by Mahan (*58*). The relative merits of the iodine-starch and the *o*-tolidine procedures for determining chlorine dioxide were discussed by Ingols and Ridenour (*39*). A review of the various methods for determining chlorine residuals was given by West (*107*).

Gad (*26*) reported a simplified procedure for using *o*-tolidine in the free chlorine test by adding to a 100-ml. sample a few drops of sodium pyrophosphate buffer and 1 ml. of *o*-tolidine and comparing with standards made from copper sulfate, potassium dichromate, and sulfuric acid. Trakhtman (*100*) observed that a change in pH affects the free chlorine content of water. He recommended that chlorine be determined without adjustment of pH.

DISSOLVED OXYGEN

An evaluation of the methods for determining dissolved oxygen in deaerated boiler feedwater was made by Sebald (*88*). The study includes the effects of such interfering substances as ferrous sulfate, ferric sulfate, sodium sulfite, and tannic acid. Gurney and Young (*31*) recommended two procedures for residual dissolved oxygen in boiler feedwater in the presence of sodium sulfite. Both are modifications of the Winkler test, differing only in the manner of adding iodine to the samples.

Killner (*45*) described a "tablet" method for determining dissolved oxygen in deaerated water by the Winkler procedure using standard tablets instead of burets and standard solutions. It is noted that untrained workers can determine from 0.02 to 0.10 ml. per liter of oxygen by this method.

A polarographic method for determining dissolved oxygen in water and sewage was reported by Moore, Morris, and Okun (*62*). Results on sewage indicate 0.7 p.p.m. higher than by the Pomeroy-Kirschman modification of the Winkler test. The dropping mercury electrode has been reported by Spoor (*94*) for the measurement of dissolved oxygen in flowing water.

According to Tuve (*101*), certain reagents such as pyrogallol having definite thresholds of sensitivity to oxygen can be sensitized in such a manner as to make them useful for colorimetric analysis of small traces of dissolved oxygen (less than 0.01 ml. per liter). Patrick and Wagner (*69*) described a method using a conductivity cell with mercury electrodes in which there is no flow of current unless some oxygen is present. The use of electrochemical cells to determine dissolved oxygen was also reported by Tödt (*99*), with reference to the measurement of rates of corrosion.

BIOCHEMICAL OXYGEN DEMAND AND OXYGEN CONSUMED

The B.O.D. test continues to be used by most investigators as a measure of the degree of pollution of water, even though it is not a precision test and is not suitable for all types of waste materials. Modifications of both the procedure and equipment are constantly being made.

The tendency of some waters to nitrify or denitrify during incubation can be reduced or prevented by the addition of methylene blue, according to Abbott (*1*, *2*). The methylene blue is stated to have a bacteriostatic effect. A direct method for determining the oxygen requirement of waste waters was described by Nesmeyanov (*64*). The absorption of oxygen is determined by measuring manometric pressure changes in a closed system.

A reflux method for determining oxygen consumed was reported by Moore, Kroner, and Ruchhoft (*63*). The quantity of oxygen consumed by several organic substances was determined by refluxing the sample for 2 hours with potassium dichromate and sulfuric acid and titrating the excess dichromate with ferrous ammonium sulfate using *p*-phenanthroline ferrous complex as indicator. Chloride interferes, but suitable correction can be made.

Pilc (*77*) described an improved Kubel-Schulz method for oxidation of organic matter in aqueous solutions by potassium permanganate.

COLOR AND TURBIDITY

The accurate determination of color in turbid waters that do not settle clear has long been a problem. Lamar (*51*) reported that 1 ml. of a strong solution of calcium chloride will effectively remove the turbidity without destroying or removing any of the true color of the solution.

Unusual accuracy in the determination of extremely low concentrations of coagulated material passing water plant filters was reported by Baylis (*7*). The method is based on the effectiveness of absorbent cotton in filtering out any coagulated matter in the water. Vibert (*104*) reviewed the various procedures for turbidity reported in the literature.

ORGANIC SUBSTANCES

The accurate determination of phenols, phenol derivatives, and other organic compounds in water is becoming increasingly important. Ettinger and Ruchhoft (*24*) investigated the determination of phenol and structurally related compounds by the Gibbs method. By applying refinements to the method an accuracy of about 2% was obtained in concentrations of 100 parts per billion.

Abnormally large values for phenol were found by Könen (*48*) in a river water below a paper mill. He concluded that other substances in the waste water were reacting like phenol with diazotized sulfanilic acid, and recommended separation of phenols from lignin sulfo acids prior to analysis.

Headington and Sassaman (*36*) described a procedure for determining low concentrations of chlorinated phenol derivatives. These materials can be determined with an accuracy of ±2 p.p.m. by a quartz spectrophotometer utilizing the strong ultraviolet absorption of aromatics.

A method for determining the products of acidic hydrolysis of organic matter (especially pentosans) in natural water was reported by Skopintsev (*91*). Van Beneden (*102*) studied several existing methods for determining organic matter in water and decided that the Palmer or Vande Velde procedure is preferred.

Kirschman and Pomeroy (*46*) described a wet-extraction method using chloroform to recover oil from oil-field waste waters. An accuracy of 1 p.p.m. in the range 3 to 125 p.p.m. was reported.

MISCELLANEOUS

The use of specific conductance data for checking the accuracy of water analyses was reported by Rossum (*83*). Delahay (*21*) utilized the electrical differential method of measurement in potentiometric and conductometric titrations. He indicated that these methods are especially suitable for argentometric determination of chloride.

Spectrographic methods were reported by Basavilbaso (*6*) and Scheminzky (*85*) as being suitable for analysis of water low in dissolved solids.

According to Kuper (*50*), the iodometric method for ferricyanides in water is not satisfactory for concentrations less than 10 p.p.m. He described a procedure using Turnbull blue which is applicable for concentrations from 0.2 to 10 p.p.m. Haseltine (*35*) made a study of methods of determining cyanides in waste disposal. In the 5 to 10 p.p.m. range the author recommends the Eldridge acetone–sulfur–ferrous nitrate colorimetric method.

Adamovich and Rybnikova (*4*) determined small concentrations of arsenic in water by treating the samples with ammonium iron alum, dissolving the precipitate containing the arsenic in acid, treating with copper sulfate and sodium hypophosphite, and comparing with standards. A sensitivity of 0.01 mg. is claimed. Gorgy, Rakestraw, and Fox (*30*) used the method of Jacobs and Nagler to determine arsenic in sea water.

The total cation content of water was determined by Hoek (*38*) using one of the commercial cation exchange resins. Lur'e and Stefanovich (*57*) employed cation organolites to remove calcium and magnesium which are subsequently recovered and determined. Sulfate is determined in the filtrate by titrating with standard alkali.

A critical review of the analysis of boiler waters was made by Pieters (*76*). Kroener (*49*) described a new graph for the examination of boiler feedwater and boiler water using results of alkalinity titrations. Janssen (*40*) conducted a survey on improved electrical methods for analyzing water with special reference to boiler waters.

Mika (*60*) discussed the use of photometric indicators in titrimetric analysis. Orchin, Wender, and Friedel (*65*) demonstrated that deuterium in water can be determined with extreme accuracy in a mass spectrometer by conversion of deuterium to methyl deuteride.

During the past year a bibliography on water and sewage analysis by Weil *et al.* (*105*) was published, which gives over 2500 references to analytical procedures in these fields.

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ORGANIC MICROCHEMISTRY

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IN KEEPING with the policy of Analytical Chemistry to continue the review of analytical chemistry on a yearly basis (*105*), the review for 1949 was prepared. As expected, the number of papers increased. Emphasis was given to methods of analysis that extend microchemical procedures for determining single compounds in mixtures. That the procedures for elemental organic analyses can be improved is shown by the large number of new and modified methods reported.

The American Chemical Society Committee on Standardization of Microchemical Apparatus critically examined different apparatus which it thinks should be standardized for the benefit of both the analyst and the manufacturer. Further collaborative work was done leading to the establishment of standard microprocedures for the Association of Official Agricultural Chemists.

METHODS OF ANALYSIS

Carbon and Hydrogen. The "unpacked" tube is probably the most interesting feature of the carbon and hydrogen methods of analyses reported. Conventional copper oxide, platinum, and other catalyst fillings and asbestos separators have been eliminated, and instead quartz wool is used. Whether the quartz acts as a catalyst or merely as a heater for the passing gases is not certain. The "unpacked" tube requires a much higher rate of oxygen flow and higher combustion-tube temperatures. Colson (*15*) used 40 ml. of oxygen per minute and 800° C.; granular silver maintained at 600° C. was used to remove the halogens and sulfur, and lead dioxide held at 180° C. was used to remove oxides of nitrogen from the combustion products. Korshun and Klimova

(*59*) used a similar rapid rate of oxygen flow but a temperature of 900° C. Solid samples were placed in a special microthimble; volatile liquids were put in a coiled capillary tube. "Unpacked" combustion tubes promise greater rapidity of analysis. To make the procedure generally applicable, however, further studies are required to ascertain the correct combination of size of tube, rate of oxygen flow, rate of volatilization of sample, and temperature of combustion.

Of all the microprocedures reported for carbon and hydrogen it was claimed that the packed-tube method of Fischer (*26*) offered the greatest improvement in accuracy. With his semiautomatic apparatus, sensitized catalysts, and 10- to 20-mg. samples, an accuracy of ±0.02% was reported. Lescher (*68*) described a semimicro modification, especially adapted to the analysis of liquid samples, in which the liquid was slowly vaporized and burned in a flame at the tip of an ampoule container. As in the unpacked-tube methods, the rate of oxygen flow was much higher than normal. Changes in combustion-tube filling were suggested by Bennett (*6*), who placed a 180-mm. section of "reduced" copper in front of a 150-mm. section of copper oxide, making it unnecessary to use lead dioxide with nitrogenous organic compounds. Combustion was carried out in a stream of nitrogen containing a small amount of oxygen. The reported results were high, but all were within the acceptable range. Heron (*46*) recommended an increase in the quantity of lead dioxide or a liquid absorber to remove more effectively the oxides of nitrogen. La Force, Ketchum, and Ballard (*65*) successfully analyzed carbonates, cyanides, and alkali or alkaline-earth organic salts for carbon by covering the sample with sodium bisulfate, then performing the combustion in the usual manner.

Two new methods employing the Van Slyke–Folch wet combustion reagents for carbon were reported in which carbon is collected as barium carbonate. Farrington, Niemann, and Swift (*24*) described a method that eliminates the need for the Van Slyke manometric apparatus; Lindenbaum, Schubert, and Armstrong (*69*) changed the usual procedure to make it applicable to analyses involving isotopic carbon.

Goulden (*38*) used a macrobalance with the method of Sucharda and Bobranski. The time required for an analysis is shortened by increasing the rate of oxygen flow and the amount of copper oxide filling. The probable sources of error in the semimicromethod of ter Meulen and Heslinga were discussed by Guzman (*41*). Renard (*88*) reviewed the literature describing open and closed absorption tubes. For determination of hydrogen alone, Pepkowitz and Proud (*85*) proposed a gasometric micromethod which depends on diffusion of the hydrogen from organic and inorganic compounds from a sealed iron capsule into a simple vacuum system. Accuracies comparable with those of standard combustion procedures were reported; none of the other elements interfered.

Nitrogen. KJELDAHL. Report of a collaborative study by Willits and Ogg (*106*) emphasized the wide discrepancy between nitrogen values for a refractory compound (nicotinic acid) obtained by different analysts. Good nitrogen values, however, were obtained by some of the procedures. White, Secor, and Long (*104*) accurately analyzed amino acids containing refractory nitrogen by digesting with a mercury catalyst. Although there is a tendency to omit selenium, Rauen and Buchka (*87*) claimed that 1-hour digestion after the mixture clears is sufficient for lysine and proteins containing lysine if sulfuric acid containing 0.7% selenium oxide is used. One point which most workers have not stressed but which appears to be critical is the temperature of the digestion mixture.

A modification of the Parnas apparatus reported by Johanson (*51*) includes a steam jacket for distillation, removal of spent liquor, and simple construction and assembly. Machemer and McNabb (*71*) found an average error of approximately 0.1% in distillation of ammonia into 4% boric acid and titration with methyl red indicator.

Day, Bernstorf, and Hill (*19*) suggested a modification of Sobel's microaeration technique in which aeration is carried out at 70° C. Kotlyarov (*60*) proposed a new formula for calculation of nitrogen by which the colorimetric micromethod can be used to determine 10 to 100 micrograms with an accuracy of 2 to 3%.

DUMAS. Most of the changes in the Dumas procedure proposed have been in the apparatus rather than in the technique. After a critical study, Bussmann (*12*) recommended the Zimmerman method because it reduces the possibility of errors due to leakage of air into the system under reduced pressure. Heron (*46*) proposed a banded tube filling of alternate layers of coarse and fine copper oxide for volatile compounds low in nitrogen. Brancone and Fulmor (*11*) raised the temperature of the burning furnace from 700° to 900° C. to aid in the decomposition of refractory ring compounds.

Carbon dioxide generators were described by Schöniger (*89*) and Furter and Bussmann (*30*). The AMERICAN CHEMICAL SOCIETY Committee for the Standardization of Microchemical Apparatus (*16*) described a sturdy all-metal needle valve that allows the same precise control of the rate of gas flow as does the more fragile Hershberg-Southworth valve. A weight nitrometer that eliminated disassembly was described by Koch, Simonson, and Tashinian (*56*).

Halogens. Schumb and Radimer (*91*) reported a method for determining fluorine in volatile compounds in which the sample is decomposed with moist oxygen in a platinum tube at 1100° C. The absorption unit is saran tubing and the final measurement is made colorimetrically. Here, as in the carbon and hydrogen determinations, a high ratio of oxygen to oxidizable material is important. Lingane and Small (*70*) suggested an interesting coulometric method for determining halide ions by which either a single halide or mixtures of iodide and bromide or iodide and chloride are determined. This method measures the electricity required for the quantitative reaction of the halide ion with a silver anode having controlled potential. Kirsten (*54*) improved his titrimetric procedure for chloride and bromide ions by substituting mercuric nitrate for the mercuric acetate previously used.

Two papers described determination of bromine. One, by Alicino, Crickenberger, and Reynolds (*1*), is based on an iodometric procedure that reduces the time required for analysis. The other, by Daudel, Flon, and Herczeg (*18*), uses the Parr bomb technique to destroy organic matter so that radioactive bromine can be measured more accurately.

Spectrophotometric methods for iodine were more involved than the volumetric procedures but were applicable to the analyses of smaller amounts of iodine. Custer and Natelson (*17*) pointed out that ultraviolet spectrophotometric measurements of solutions of elemental iodine in benzene, toluene, and potassium iodide permitted determination of as little as 0.2 microgram. Shakrokh and Chesbro (*92*) measured iodine spectrophotometrically after chromic acid oxidation of organic matter, reduction by phosphorus, oxidation to the iodate by chlorine, and reduction to free iodine by potassium iodide in acid solution. Gross, Wood, and McHargue (*40*) used a similar series of reactions but added starch and measured the starch-iodine blue complex by its light absorption in the visible region.

The volumetric methods of Grangaud (*39*), Schulek (*90*), and Lacourt and Timmermans (*64*) used the reactions silver iodate and filtration, chlorine water, and Viebock and Brecher's bromine method to obtain the iodine as iodate. The iodate was determined iodometrically with thiosulfate. The method of Lacourt and Timmermans can be used for simultaneous determination of carbon, hydrogen, and iodine, but a long time is required for iodine analysis.

Intonti and Gargiulo (*50*) determined two of the three halogens (chlorine, bromine, or iodine) simultaneously from the weight of the two silver salts and from the amount of the silver used, which was determined by either gravimetric or volumetric analyses.

Metallurgia published some critical reviews of micromethods for particular elements. One, by Beaucourt (*5*), is a review of procedures for determination of halogens.

Sulfur. A gravimetric method by Stragand and Safford (*99*) is simple, direct, and generally applicable to organic sulfur analysis. The sulfur trioxide from catalytic combustion of organic material is caught on silver gauze, and its weight determined; or if halogens are present, the silver sulfate is dissolved in water, and the amount of sulfur is calculated from the loss in weight.

Two methods were reported for determining sulfur in compounds in which sulfur is readily converted to the sulfide. Klimenko (*55*) used alkali to convert the sulfur in proteins and tissues to sulfide or hydrosulfide. These are converted to sulfate, which in turn reacts with barium chromate; the liberated chromic acid is measured iodometrically with thiosulfate. Acid was used by Pepkowitz (*84*) to liberate hydrogen sulfide, which was distilled into standard calcium hypochlorite; the excess hypochlorite was determined iodometrically.

Two critical reviews, one, by Lamo (*66*), of semimicromethods and the other, by Thomson (*100*), of micromethods, discuss gravimetric as well as direct and indirect volumetric methods of sulfate analysis.

Unsaturation. In the past, unsaturation has been determined largely by macroprocedures using halogenation methods; there have been relatively few analyses by direct hydrogenation. Hydrogenation has two advantages; it is not empirical, and it is satisfactory for conjugated unsaturation, for vinyl and allyl compounds, and for double bonds that are inaccessible to halogens because of steric hindrance. Microhydrogenation is less time-consuming and less subject to interference by catalyst poisons. Ogg and Cooper (*81*) presented a simplified apparatus and procedure for quantitative catalytic microhydrogenation. For microhalogenation, Phillips and Wake (*86*) used a special reaction flask and technique. A method for determination of the iodine number of lipides in blood serum was described by Giraut-Erler and Grimberg (*32*).

Acetyl. Elek and Hart's method for acetyl determination was modified by Bradbury (*10*) to eliminate the sulfur dioxide correction and avoid errors due to carbon dioxide.

Water. Determination of water in small amounts of material, by the calcium carbide method was described by Gorbach and Jurinka (*35*). Fischer (*27*) suggested three methods for detection of water: Potassium lead iodide in gasoline when heated with a trace of moisture or water of crystallization forms yellow lead iodide and bubbles; calcium carbide emulsion in peanut oil when heated with water leads to bubbles that remain visible after cooling; and phosphoric acid formed by adding traces of water to a gasoline solution of phosphorus pentoxide and bromocresol purple causes a change in the color of the indicator.

Alcohols. A quantitative colorimetric microdetermination of methanol was reported by Boos (*9*) to be rapid and specific. Opfer-Schaum (*82*) detected glycerol in mixtures by forming acrolein hydrazone and determining its eutectic temperature with *p*-nitrophenylhydrazine microscopically. De Meio (*20*) described a microextraction procedure for separating phenol before determining the phenol spectrophotometrically.

Acids. Although organic acids are now detected and determined largely by chromatographic techniques, some purely chemical methods have been reported. Kometiani and Sturua (*57*) described a micromethod for citric acid, and Volpi (*103*) described a method for detection of succinic acid in the presence of aconitic and tricarboxylic acids.

Other micromethods reported include a polarographic method for amino acids (*74*) and a new procedure for tryptophan (*95*).

peri-Naphthindantrione hydrate was substituted for ninhydrin in amino acid analysis by Moubasher and Awad (*79*). Steele, Sfortunato, and Ottolenghi (*94*) applied Schneider's method to the microanalyses of nucleic acids. Tracey (*101*) developed a manometric method for measurement of uronic acids.

Carbohydrates. Methods for determining glucose and mannitol in blood were described by Mosto and Cavanna (*78*) and Hamburger *et al.* (*44*), respectively. Mosto and Cavanna's paper also includes a method for urea analysis in which the urea is measured by nesslerization after treatment with urease. Use of partially hydrolyzed dextran as a substitute for blood in the treatment of shock led Hint and Thorsen (*47*) to develop a micromethod for dextran in blood.

Miscellaneous. 1-Nicotine was recovered from animal tissue and determined by Trim (*102*), who observed a linear relation between color and concentration over the range 1.5 to 20 micrograms of nicotine per milliliter of solution.

Shkitin (*93*) developed a method for identifying azo dyes on paper or thread.

Hamburger and Rasch (*43*) compared different micromethods for determining 17-ketosteroids in urine. Methods were reported for riboflavin (*29*), phosphatase (*36*), diastase (*77*), albumin (*23*), and globulin (*13*). In addition, Kunzmann (*62*) discussed the use of micromethods in the cosmetic industry, and Kretchmer (*61*) reviewed the application of micromethods in lipide chemistry.

Molecular Weight. An isothermal diffusion method was proposed by Wright (*108*), in which solutions of a known and an unknown were placed on separate pieces of filter paper and left with their vapor phases in common. The molecular weight of the unknown was calculated from the weight of solvent on the two papers.

Wilson (*107*) published a comprehensive review of molecular-weight methods. With Magee (*73*), he recommended that a cloth sleeve be used on Beckman microthermometers to minimize temperature fluctuations encountered in ebullioscopic methods.

APPARATUS

Balances. A submicrobalance of the torsion type and some techniques and applications were described by Ingram (*48*, *49*). Stock and Fill (*98*) controlled the swings in semimicro weighings by an air jet. Feuer (*25*) discussed a new type microbalance utilizing radiation from radioactive material, with a load capacity of 25 to 50 grams per pan and with high sensitivity and stability.

Miscellaneous. Modifications of the horizontal burets of Conway and Benedetti-Pichler have been proposed (*45*, *58*, *63*), together with three new displacement-type microburets (*31*, *97*). Two new stirring devices for microtitrations have been described (*14*, *96*).

Several distillation apparatus have been reported for volumes from 0.1 to 4.0 ml. with improved means of fraction recoveries (*4*, *7*, *37*, *42*, *67*). Three metal block-type melting point apparatus, one gas and two electrically heated, have been described (*72*, *75*, *83*); all use an optical magnification system for detecting the melting point, and that of Matthews (*75*) is equipped with a cooling device. An apparatus for microsublimation using an electric light as source of heat was proposed by Meyer (*76*).

A pipet (*33*) for spray rinsing of pipets with a measured volume of liquid has been described, and the drainage of micropipets has been studied (*3*). Other apparatus include a micromuffle (*34*), high-temperature coil and ring gas burners for microcombustions (*2*), a liquid-liquid extractor (*53*), microadapters for the Evelyn colorimeter (*28*) and the Beckman pH meter (*21*), and a thermostatically controlled micropolarimeter tube (*52*). Apparatus for making vapor pressure measurements (*8*, *80*) have been proposed, and a versatile microapparatus for filtration, extraction, and distillation has been designed (*22*).

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The Importance of Analytical Techniques

Illustrated by the Management of a Broad Catalyst-Testing Program

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Basic critical evaluation of available analytical tools is a necessary prerequisite to initiation of an industrial research program. Preliminary research into test and analytical procedures, as a logical approach to a field of investigation, is exemplified by the experiences introductory to a recent broad catalyst-testing program. The problems in the development of adequate routine methods prior to these studies in the "butadiene-from-ethyl alcohol" process demonstrate the prime importance of establishing a sound basic testing and analytical laboratory prior to launching a research project.

BEFORE any research project is undertaken, the aims of the sponsor, time limitations, and budget allotment must be viewed in the light of limitations of available tools. The adequacy of tools, both testing and analytical techniques, should be evaluated critically and if they are not compatible with the time and budget restrictions, the latter must be made more flexible or the responsibility for success should not be assumed. Stated conversely, testing and analytical techniques must be prime considerations in fixing the time and budget, never vice versa.

Regardless of the urgency of the project—e.g., a problem pertaining to an operating commercial process—no sound and useful results are likely without adequate basic analytical procedures. Where the latter are inadequate, a more or less indefinite preliminary period of time must be stipulated for development of sufficiently accurate methods prior to initiation of the testing or development program. Although these statements are almost pedantic, it is the paramount purpose of this discussion to demonstrate their practicality and essentiality, for they are too often neglected.

In many instances the analytical problems cannot be defined clearly in advance. In these cases the analytical needs crystallize as preliminary work proceeds. At some early stage a pause is required, preceding the initiation of a program of testing operating-variable effects of the chemical reaction or process. The point which requires emphasis is that this pause, if for no other reason, is mandatory for establishing sound analytical methods. The ideal situation is that in which all preparatory analytical developments can be anticipated and solved beforehand. But, where this is not possible, there should be definite recess points where advance should cease until sound analytical data are certain.

Often the development program is started under the assumption that analytical developments can be carried forward simultaneously. This too often leads to conflicting indefinite implications, misconceptions, and arguments, which in turn conduces to expending excess effort and experimental work before harmful ill-founded trends in thinking and doing can be eliminated. It is indeed the exception when time is gained by not awaiting basic analytical development early in any research program, whether practical and fundamental. The number of possible interpretations of a mass of data from studies of operating variables is inversely proportional to the soundness of the analyses on which the data are based.

An undertaking of a catalyst-testing program in the process for production of butadiene from ethyl alcohol is discussed herein to exemplify the critical evaluation of test and analytical procedures which should precede acceptance of a project involving a large schedule of routines. Relatively low yields (about 63% of theory) realized in operation of the Defense Corporation plants led to establishment of a fellowship at Mellon Institute in 1944. (Actual plant variations in yields were ±2%.) It was requested that 1000 new catalytic combinations per year be tested as part of the program of studying methods for effecting improvement in the commercial yields of butadiene. A catalyst for which a 2% higher yield could be established would bring about a tremendous savings in a critical raw material—over 40,000,000 pounds of ethyl alcohol annually for the three ethyl alcohol–butadiene plants.

OUTLINING NEW PROGRAM FOR BUTADIENE FROM ETHYL ALCOHOL PROCESS

The Carbide and Carbon process (*3*) for the manufacture of butadiene from ethyl alcohol was utilized to supply the major portion of the emergency requirements for this chief essential raw material in the production of synthetic rubber. In this process, part of the ethyl alcohol was dehydrogenated to acetaldehyde and subsequently ethyl alcohol–acetaldehyde mixtures were processed over tantala-silica catalyst at 350° C. at about 7 seconds' contact time. The over-all chemistry is represented as follows: $CH_3CHO + C_2H_5OH \longrightarrow C_4H_6 + 2H_2O$ (*6, 8*). Butadiene was separated from the catalyzate and purified; unreacted ethyl alcohol and acetaldehyde were recovered and recycled.

This process represents an achievement, because it was developed under stress and there was not sufficient time for development of analytical methods adequate for use in the usual routine laboratories. Relatively skilled technicians were required to obtain sound analytical data on which to base design considerations. For example, per-pass and ultimate yields of butadiene were established by quantitative formation and isolation of the solid tetrabromobutane; and the percentage of unconsumed ethyl alcohol and acetaldehyde depended on chemical analyses not specific for these constituents in the presence of certain by-products. These by-products in the converter effluents were not quantitatively separable by distillation, apparently because of azeotrope formations.

The scope of the suggested catalyst testing program (1000 catalysts per year) together with budgetary considerations necessitated, first, an accelerated schedule of catalyst preparation and testing, and, secondly, analysis of materials by relatively untrained technicians because of the emergency shortage of technical personnel. Without good reproducibility of results, interpretations of activities of competitive catalysts might be misleading. Whether increases in yield of small percentages could be recognized had to be established by a preliminary critical examination of existing methods and procedures, in both testing and analytical work. The first step in evaluation of analytical methods was the establishing of quantities of materials to be handled. These quantities in turn were dependent on the equipment to be employed.

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Selection of equipment for the catalyst-testing portion of the program was based on practical considerations of time, personnel, and funds available; analytical requirements were then fixed by quantities of resultant materials and minimal accuracies calculated as necessary for precision of yield data.

SELECTION OF TEST EQUIPMENT AND PROCEDURE

The prime considerations in the selection of equipment were the volume of new catalysts to be prepared and the volume of liquefied effluent available therefrom in a run of practical duration at the commercial feed rates [0.4 to 0.6 liquid hourly space velocity (l.h.s.v.)]. Liter quantities of catalyst were feasible from the standpoint of preparation and analysis of ten catalysts per week with eight to ten persons. This permitted eight runs with 125 ml. of catalyst per test. From this amount (125 ml.) of catalyst, a 400-ml. volume of liquid products was obtainable in 8 hours at a feed rate of 0.4 l.h.s.v. It was established that this volume of effluent was readily distilled with a laboratory column (12 to 18 plates) during one 8-hour work period to give a practical separation of products into overlapping fractions containing, respectively, butadiene, acetaldehyde, and ethyl alcohol. Therefore, laboratory systems with a catalyst capacity of 125 ml. were selected from several available systems for preliminary critical calculations. One of these units is represented by the diagram shown in Figure 1.

The test procedure, described elsewhere (*1*), is briefly as follows: Four hundred milliliters of mixed ethyl alcohol–acetaldehyde feed are passed over 125 ml. of catalyst during a period of 8 hours; the effluents are liquefied with dry ice; the uncondensable gas is collected over a saline solution; and the carbon deposition on the catalyst is determined after the end of the run. The material balance is determined on the basis of these three values—i.e., liquid, gas, and carbon.

ESTABLISHMENT OF REQUIRED ACCURACIES

Analytical procedures and test methods employed in the original development of this butadiene process were made available to the fellowship by the Carbide and Carbon Chemicals Corporation. Although these methods had served for developing the process through the pilot-plant stage, their adequacy was doubtful for the new project where recycle could not be utilized to minimize effect of analytical errors. It was calculated that their precision had to lie within ±1% if yield data were to be sound enough to indicate improved catalysts. This ±1% is predicated on ±1% material balances leading to the permissible or acceptable maximum of ±2% reproducibility of the over-all test and analytical procedure. This ±2% reproducibility represents the maximum limits of the variations in test data that would carry conviction in view of experienced variations in commercial monthly production figures.

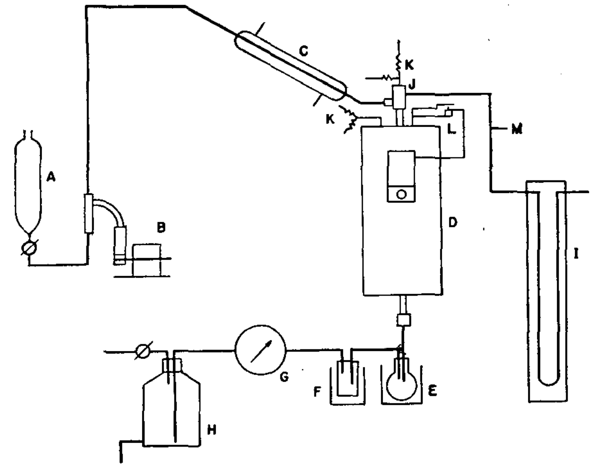

Figure 1. Flow Diagram of Laboratory Apparatus

A. **Feed reservoir**
B. **Pump**
C. **Vaporizer**
D. **Furnace**
E. **Product flask**
F. **Dry ice trap**
G. **Wet test meter**
H. **Gas collection system**
I. **Manometer**
J. **Catalyst tube**
K. **Thermocouples**
L. **Temperature regulator**
M. **Nitrogen line**

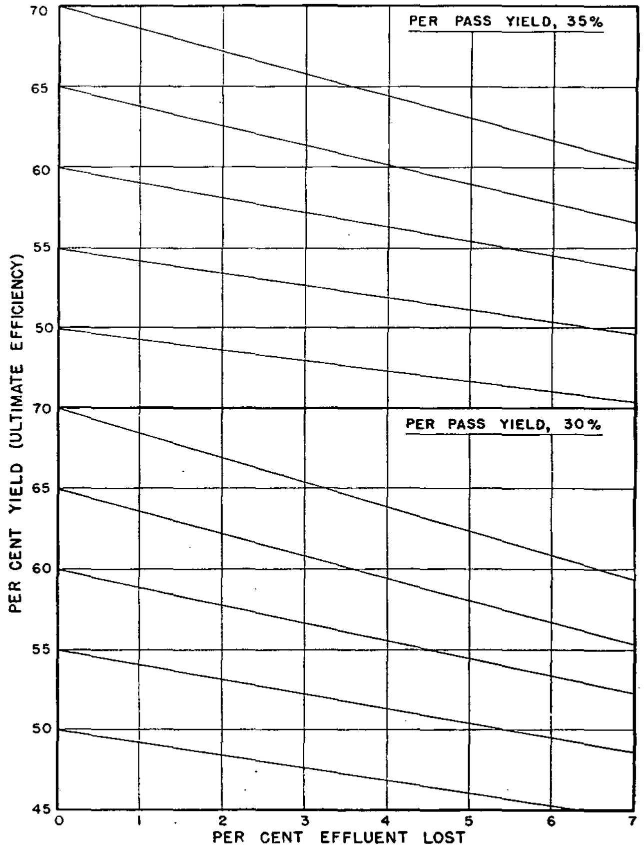

Figure 2. Effect of Material Losses on Calculations

For accurate per-pass and ultimate yield data a minimum of three components had to be known with accuracy. The per-pass yield was calculated as follows:

$$\text{Mole \% per-pass yield} = \frac{\text{moles of } C_4H_6 \text{ formed} \times 200}{\text{moles of } C_2H_5OH \text{ fed} + \text{moles of } CH_3CHO \text{ fed}}$$

The ultimate yield was similarly calculated:

$$\text{Mole \% ultimate yield} = \frac{\text{moles of } C_4H_6 \text{ formed} \times 200}{\text{moles of } C_2H_5OH \text{ reacted} + \dfrac{\text{moles of } CH_3CHO \text{ reacted}}{0.92}} =$$

$$\frac{\text{moles of } C_4H_6 \text{ formed} \times 200}{(\text{moles of } C_2H_5OH \text{ feed} - \text{moles of } C_2H_5OH \text{ out}) + \dfrac{\text{moles of } CH_3CHO \text{ feed} - \text{moles of } CH_3CHO \text{ out}}{0.92}}$$

The factor 0.92 was derived from the 92% yields of acetaldehyde in the dehydrogenation of ethyl alcohol, so that the yield of butadiene was based on ultimate consumption of ethyl alcohol in the whole process. Ethyl alcohol and acetaldehyde analyses entered into the calculations twice (feed and effluent), and sound basic values for these components were therefore necessitated.

Correlations of errors in analysis and test runs with the effects on final yield data were the first considerations in evaluation of available procedures. To establish accuracies required for these three chief analyses, if ultimate yields were to be reproducible to ±2%, a series of curves, typified by Figure 2, were drawn to show the effect of handling and analytical losses on yields. These curves were based on actual quantities to be involved in the above-outlined test runs. A major quantitative implication of Figure 2 (for the above-fixed 400-ml. quantities of feed per run) was that a loss of about 8 ml. (7 grams) of feed or product would invalidate the test, in that ultimate yields would be adversely affected to an extent greater than 2% even before the errors of analysis were encountered.

A study of the whole test procedure revealed that errors or losses, which were entailed in establishing the recovered amounts of the several constituents, could be realized in (*a*) the test run, (*b*) distillation of the products, and (*c*) the analysis of the various fractions from the distillation. Losses in (*a*) or (*b*) could be eliminated only by careful recoveries of materials from the test run and distillation. Practically speaking, this meant the careful determination of material balances in these two operations and discarding those runs that showed losses exceeding some established limit. It can be seen that a deviation of ±1% in material balances leaves an accuracy of only ±1% permissible for subsequent analytical procedures. Catalyst holdups and carbon on catalyst had to be taken into account. Distillation holdups likewise had to be determined and allowed for.

Recoveries of 100 ± 1% eventually were established experimentally as the best to be expected routinely from the above-described test run and distillation. Errors or losses traceable to analytical procedures (*c*) therefore had to be held at the preliminarily assigned minimum, no more than ±1%, if the combined errors from (*a*), (*b*), and (*c*) were to be maintained within ±2%.

The greatest interest in evaluation of new catalysts centered in those of initial activity in the range of 25 to 35% yield of butadiene per pass. Catalysts which gave lower per-pass yields, even though accompanied by higher ultimate yields, were of secondary concern, for their use in the plants would entail a sacrifice in production. Figure 3 shows the effect of a summation of errors or losses incurrable in the three steps above (*a*, *b*, and *c*) over the range of 5 to 40% yields per pass as reflected by ultimate yield calculations. It is clear that, in the range above 30% per-pass yield, the effects of errors fortuitously are decreasingly small. It is also plain that accuracies of the three individual determinations (butadiene, ethyl alcohol, and acetaldehyde) must be considerably below 1%, because the cumulative error for the three analyses (*c*) must be below ±1% in a run giving 35% yield per pass, if the ultimate yield is to be established at, say, 63 ± 2%.

SELECTION AND IMPROVEMENT OF METHODS FOR A ROUTINE LABORATORY

The apparent simplicity and straightforwardness of the separation and analysis of the several fractions were somewhat misleading. It was found that modifications and strict specifications had to be established for each simple step of the analytical methods before essential reproducibility could be attained. Preliminary studies of the methods utilized for the development of the process (with skilled analysts having B.S. or M.S. degrees plus several years in analytical work) were carried out in the routine laboratory (with less skilled analysts of less than chemical graduate training and no practical experience). The errors realized were found too great for the requirements demonstrated by Figures 2 and 3. The procedures for collecting and working up the products were adequate, however, for good material balances. (Storage and handling of the liquefied effluents in dry ice systems had to be done with care to avoid dissolving carbon dioxide, because the solubility of carbon dioxide is high in mixtures containing C_4 hydrocarbons.) The effluent from testing was obtained as a small amount of gas (noncondensable at dry ice temperatures) and a large amount of liquid. The gas density was obtained (for material balance only) and the liquefied product was fractionally distilled (12- to 18-plate packed columns) to obtain the fractions distilling as follows:

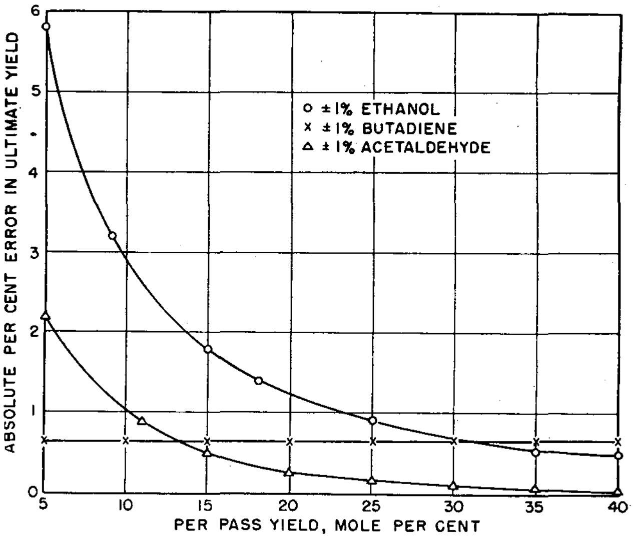

Figure 3. Effect of Total Errors of Recovery and Analysis on Ultimate Yield Calculations for Per-Pass Yield Range of Interest

1. Gas
2. −46° to +13° C.
3. +13° to 30° C.
4. 30° to 90° C.
5. Residue

Subsequent analyses of these fractions by the old procedures were not adequate. Neither the analysis of fraction 2 for butadiene (by conversion to tetrabromide) nor the analysis of fraction 4 for ethyl alcohol (by esterification with acetic anhydride–pyridine reagent, *10*) was precise to 1% of the absolute value. Acetaldehyde by the hydroxylamine–sodium hydroxide procedure to the bromophenol blue end point was the best of the three analyses, but reproducibility was still only about ±0.5%. A preliminary canvass of industrial laboratories was conducted in addition to a literature survey. The Koppers-Hinckley method (*8*) for butadiene (an improved method involving reaction with maleic anhydride) appeared to be a good possibility for the needs, reportedly attaining an accuracy of ±0.2%. However, esterification procedures for the ethyl alcohol (*2*) and hydroxylamine methods (*5*) apparently had no good alternates likely to be amenable to improvement for the purposes of the project.

Because these methods now have been adequately described in the literature they are not reviewed here; but an outline of some of the points considered will serve to show the types of things which are apt to prove troublesome and which are too often accepted from other applications without critical consideration.

Maleic Anhydride Method for Butadiene. The apparatus evolved for this determination is called the Koppers-Hinckley apparatus. The method was known at the instigation of the program, although certain factors were found to require close attention and improvement: control of concentration of the potassium hydroxide (hence vapor pressure), elimination of contact with stopcock greases and general extreme cleanliness, and frequent calibration of the nitrometer, which is attacked by the potassium hydroxide.

Phthalic Anhydride Method for Ethyl Alcohol. This method in its original form was associated with occasionally counterbalancing errors. The cause of the inherent errors had to be defined before reproducibility was possible. The following list demonstrated relevant details which it was necessary to consider and control in order to obtain satisfactory results with this method:

Anhydride concentration
Effect of water content

Deterioration of the anhydride reagent
Sampling technique
Reaction flask—effect of rubber gasket on end point and absorption of reagent by rubber gasket
Effect of aldehydes and ketones

A modified method with all-glass equipment was developed eventually by a study of synthetic samples and catalyzate. Each of the above points required strict definition and control in the modified procedure eventually employed in the laboratory.

Hydroxylamine Hydrochloride Method for Acetaldehyde and Acetal. The recyclable acetaldehyde value is derived from four different analyses (analyses of C_4 fraction, acetaldehyde fraction, ethyl alcohol fraction for acetaldehyde and/or acetal) and therefore the reproducibility of the total aldehyde is the poorest of the various analyses involved. Pertinent points considered for which strict specifications had to be established: end point and indicator, temperature of analysis, concentrations of hydroxylamine hydrochloride, and effect of other aldehydes (*6, 7, 9*).

OVER-ALL REPRODUCIBILITY OF RESULTS

Utilization of the improvements and modifications referred to the over-all reproducibility of the test procedure, distillation, and analyses confirmed the preliminary calculations with regard to required and possible accuracies. About ±1% on test and distillation and about ±1% on analysis led to ±2% over-all reproducibility. In view of agreement with plant-yield data these values were acceptable.

Twenty-one duplicate experiments (Table I) were made on a shipment of fresh commercial catalyst as received, the operating conditions being 350° C., 2.75 to 1 feed ratio, 0.4 l.h.s.v., and 12 × 1 inch (30 × 2.5 cm.) catalyst bed. Only after reaching this required accuracy of the over-all test was it considered safe to proceed with the catalyst-testing program.

During the development work on these analytical methods the project personnel was being built up for the planned testing program, and operations were started to establish practical work schedules, to acquaint test personnel with procedures, to routinize distillation techniques, and to establish attainable material balances. These preliminary runs afforded opportunity for obtaining statistical information relative to reproducibilities securable with the relatively unskilled personnel of the routine analytical laboratory employing methods before and after modifications herein discussed (Table II). The improvement in number of reliable runs was from 20 to 102 in the two series of 120 runs each.

Butadiene analyses were reliable throughout, in that the improved procedure for butadiene was available early. Per-pass yield data were good for both periods shown, in view of the fact that feed make-up was accurate, and per-pass yields depended only on accurate values for feed make-up and butadiene formed. The loss of per-pass yield data was due mainly to occasionally poor material balances. The ultimate yields were in general too irreproducible (greater than ±2% variations) when they depended on the initial unmodified analytical procedures.

Table I. Reproducibility of Results

(21 duplicate expts.)

	Mean Value, %	Standard Deviation[a] from Mean Value, %
Ultimate yield of butadiene	63.6	2.0
Per-pass yield of butadiene	35.6	2.1

[a] $\pm\sqrt{\frac{\Sigma d^2}{n-1}}$

Table II. Adoption of Modified Procedures

	Before	After
Total number of runs compared	120	120
Runs with reliable duplicate ultimate yield data[a]	20	102
Runs with reliable per-pass yield data[a]	110	108

[a] 2% or less deviation from triplicate average.

The first direct result of these developmental studies of method and procedures was the halving of the number of catalysts that could be prepared and tested under the contemplated budget. Only 500 catalysts per year could be projected under the six sets of conditions contemplated, instead of the 1000 originally requested.

Because the reproducibility of the test and analytical procedures verged on the permissible minimum, work was initiated to improve the catalyst-testing procedure simultaneous with the first year's catalyst-testing program. A new improved method (*4*) was developed, reproducibility of which was about 20% better than the procedure outlined above. [A smaller scale version (*11*) of this procedure was worked out as a screening test to minimize detailed analyses by rejecting inadequate catalysts.] This new method minimized the losses incurred in the actual catalyst-testing step. It comprised a water-scrubber-distillation step for separation of C_4 and lighter material (from effluents of the catalyst test unit) as an aldehyde-free gas fraction. The acetaldehyde and ethyl alcohol were found entirely in the aqueous bottoms from the scrubber-distillation column, and thus determination of acetaldehyde content of the butadiene fraction was obviated. These latter developments permitted an annual testing of 700 catalysts per year with the same equipment and personnel.

CONCLUSIONS

The uselessness of data obtained with inadequate test and analytical tools has been emphasized. This experience indicates that project leaders must not assume that known methods will serve for new analytical requirements, as such assumption might lead to premature launching of a program and much wasted time.

Attention to basic analytical requirements must receive a major portion of the initial effort and energy in the majority of research projects. The validity of the results and the degree of success in concluding any program, in general, can be correlated with, and even predicted by, a brief critical evaluation of the analytical requirements in comparison with the adequacy of available methods applicable thereto. Careful study directed toward improved test and analytical tools can lead to more productivity of a given group of personnel, as demonstrated by the increased number of catalysts handled in the program discussed.

It is felt that educational curricula can do much in stressing the value of analytical study in preparation for major types of research and development work. Too often analytical chemistry is viewed only as a necessary tool, responsibility for which can be assigned to less imaginative routine workers. In reality, the best training and ingenuity available must be utilized to evolve and certify adequate analytical procedures. Otherwise, sound analytical data cannot come from the routine laboratory. It is not too much to say that research can produce results only in direct proportion to the early stress placed on analytical methods and procedures.

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Infrared Spectra of Carbohydrates

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The infrared absorption curves for a number of sugars and their derivatives and for some cellulose derivatives have been obtained. Anomeric forms of various glycosides and sugar esters are readily distinguished by their infrared curves, as are the various isomeric sugars and sugar alcohols. Infrared spectroscopy is an excellent tool for the identification of sugars and for the identification of important functional groups in carbohydrate materials including cellulose. The possibility of using this tool for the quantitative determination of nitrate groups in nitrocellulose has been shown.

IN THOSE fields of chemistry in which one deals with a number of compounds of similar chemical and physical properties, infrared spectroscopy is a very useful tool for analysis and identification. Examples may be found in many papers in the recent literature, particularly in the fields of synthetic rubber and petroleum chemistry. The carbohydrate chemist has the difficult job of identifying the constituents of mixtures of chemically similar sugars or of determining certain functional groups present in small numbers in polymeric materials such as starch or cellulose. These considerations motivated the study of the infrared spectra of carbohydrates and appraisal of their usefulness as a tool for the carbohydrate chemist.

The spectra of a large number of carbohydrates and their derivatives have been obtained with a Baird infrared spectrometer. In most cases the substances were purified by recrystallization until the melting point was constant. Substances which did not crystallize were measured by squeezing the viscous liquid between two rock salt or silver chloride plates. The technique used to prepare the samples of the crystalline substances was to dissolve them in a solvent such as water or methanol, put about 2 ml. of the solution on a silver chloride window, and evaporate to dryness in a vacuum oven. Samples prepared in this manner frequently give curves containing very broad and poorly resolved bands. Much sharper and better resolved bands were obtained when the solid sample was finely ground in mineral oil by rubbing with a muller on a ground-glass plate.

A comparison of the curves obtained by these two methods of preparing the sample is shown in curve 1 (Figure 1). The mineral oil has strong carbon-hydrogen bands at about 3.5 and 7 microns, but in the regions more interesting to the carbohydrate chemist, around 6 and beyond 2.2 microns, it is transparent. Each curve is marked with a symbol which indicates how the sample was prepared; *G* indicates that it was ground in mineral oil and *E* indicates that it was evaporated on the window from solution. The letter in brackets indicates the solvent used: *W*, water; *C*, chloroform; *A*, methanol; and *P*, pyridine. Each curve is numbered and the index for the curves is given in Table I.

Curve 2 of glucose is typical of the sugar spectrum. There is a very strong band at about 3.1 microns due to the oxygen-hydrogen stretching frequency of the hydrogen-bonded hydroxyl groups, and in the region of 9 to 10 microns there are several closely spaced bands which are probably due to carbon-carbon and carbon-oxygen vibrations. The effect upon the spectrum of various functional groups which the carbohydrate chemist frequently encounters is illustrated in the next four curves. Glucuronic acid, curve 3, shows a very strong band at 5.6 to 5.8 microns, which is due to the C—O of the carboxyl group. Closer examination shows that this is actually two bands and it may be that the 5.6 band is due to a lactone carbonyl and that the 5.8 band is due to the carbonyl in a free carboxyl group. Glucal triacetate, curve 4, has no unesterified hydroxyls; hence the oxygen-hydrogen band at 3.1 microns is missing. The carbonyl band due to the acetate groups again shows up strongly and a new band at 6.05 microns appears, which is due to the ethylene linkage. The strong band at 8 to 8.2 microns is characteristic of esters.

Table I. Index of Absorption Curves

Curve No.	Compound
1	D-Mannose
2	D-Glucose
3	D-Glucuronic acid
4	D-Glucal 3,4,6-triacetate
5	D′-Methoxy-D-hydroxymethyl diglycolic aldehyde
6	Sucrose octanitrate
7	D-Ribose
8	L-Arabinose
9	D-Xylose
10	D-Galactose
11	α-D-Glucose
12	L-Sorbose
13	L-Rhamnose
14	L-Fucose
15	Maltose
16	Mellibiose. H_2O
17	Cellobiose
18	Trehalose
19	D-Lactose
20	Raffinose
21	Erythritol
22	Xylitol
23	Mannitol
24	Sorbitol
25	Fucitol
26	*i*-Inositol
27	Dulcitol
28	Arabino-γ-lactone
29	Glucono-δ-lactone
30	Methyl (1-methyl-α-D-galacturonate)
31	D-Gluco-α-heptonolactone
32	Methyl β-D-xyloside
33	Methyl α-D-mannoside
34	Methyl α-D-galactoside. H_2O
35	Methyl β-D-galactoside
36	Methyl α-D-glucoside
37	Methyl β-D-glucoside
38	α-D-Glucose pentaacetate
39	α-Cellobiose octaacetate
40	α-Cellotriose hendecaacetate
41	α-Cellotetraose tetradecaacetate
42	β-D-Glucose pentaacetate
43	Methyl α-D-glucoside tetraacetate
44	Methyl β-D-glucoside tetraacetate
45	Methyl β-D-galactoside tetraacetate
46	Levoglucosan triacetate
47	α-L-Arabinose tetraacetate
48	Sorbitol hexaacetate
49	Mannitol hexaacetate
50	3-Methyl D-glucose tetraacetate
51	Lactose octaacetate
52	D-Galactose dimethylacetal pentaacetate
53	D-Galactose diethylmercaptal pentaacetate
54	L-Rhamnose diethylmercaptal tetraacetate
55	D-Glucose diethylmercaptal pentabenzoate
56	3-Methyl-D-glucose tetrabenzoate
57	3-Methyl-D-glucose
58	2,3,4,6-Tetramethyl-D-galactose
59	2,3,4,6-Tetramethyl-D-glucose
60	2,3,4,6-Tetramethyl-D-mannose
61	Methyl tetramethyl-D-glucoside
62	Methyl tetramethyl-α-D-mannoside
63	Methyl 2,3,6-triethyl β-D-glucoside
64	Levoglucosan
65	D-Galactose oxime
66	D-Mannose oxime
67	L-Rhamnose diethylmercaptal
68	D-Galactose diethylmercaptal
69	1,2,5,6-Diisopropylideneglucofuranose
70	1,2-Isopropylideneglucofuranose
71	D-Glucosamine hydrochloride
72	Kojic acid
73	Nitrocellulose
74	Cellulose oxidized with NO_2 and nitrated, polyglucuronic acid nitrate
75	Methylcellulose
76	Cellulose acetate
77	6-Trityl cellulose
78	6-Trityl 2,3-bisphenylurethane cellulose
79	6-Trityl cellulose acetate

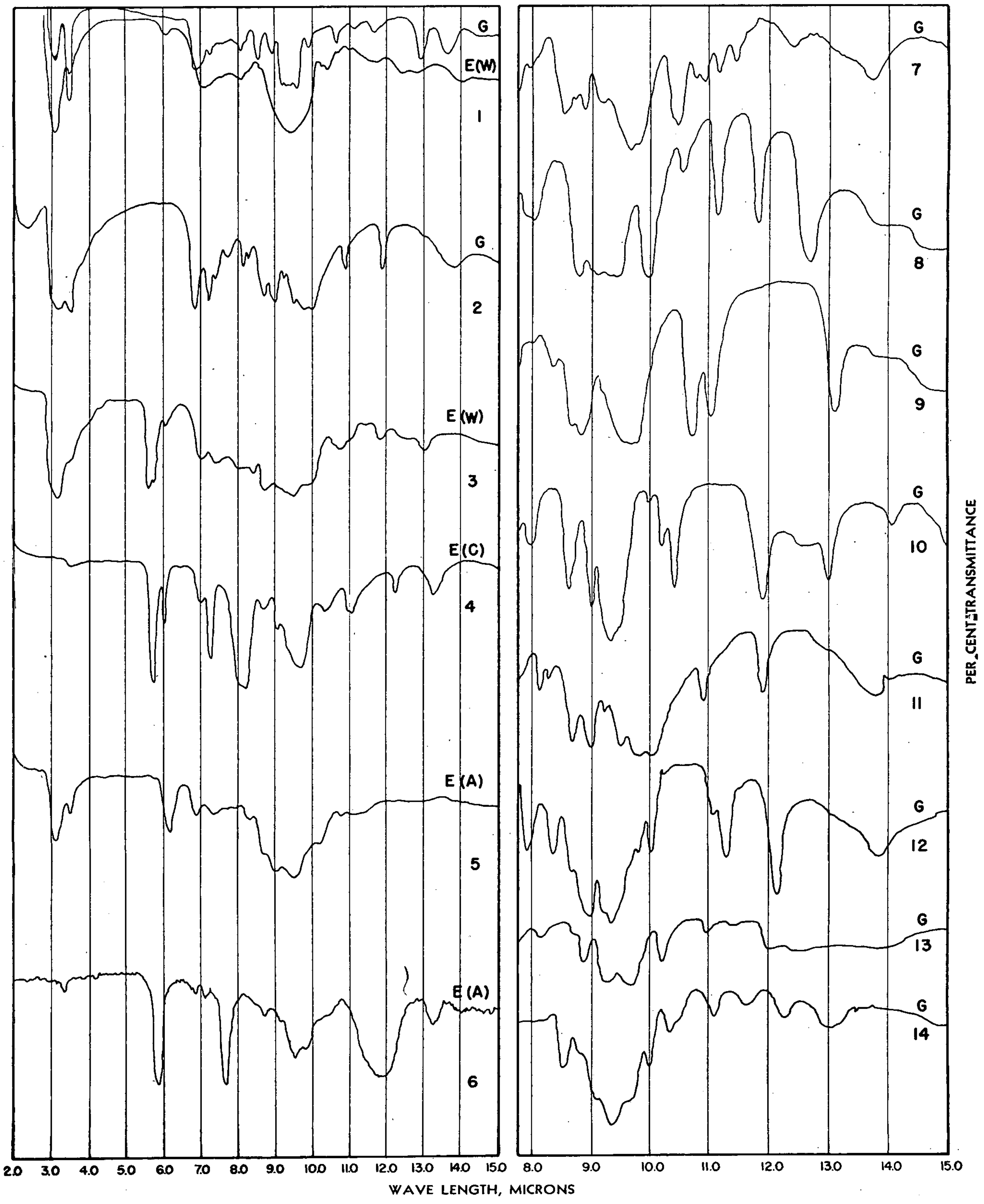

Figure 1. Infrared Spectra of Carbohydrates

1. D-Mannose
2. D-Glucose
3. D-Glucuronic acid
4. D-Glucal 3,4,6-triacetate
5. D'-Methoxy-D-hydroxymethyl diglycolic aldehyde
6. Sucrose octanitrate
7. D-Ribose
8. L-Arabinose
9. D-Xylose
10. D-Galactose
11. α-D-Glucose
12. L-Sorbose
13. L-Rhamnose
14. L-Fucose

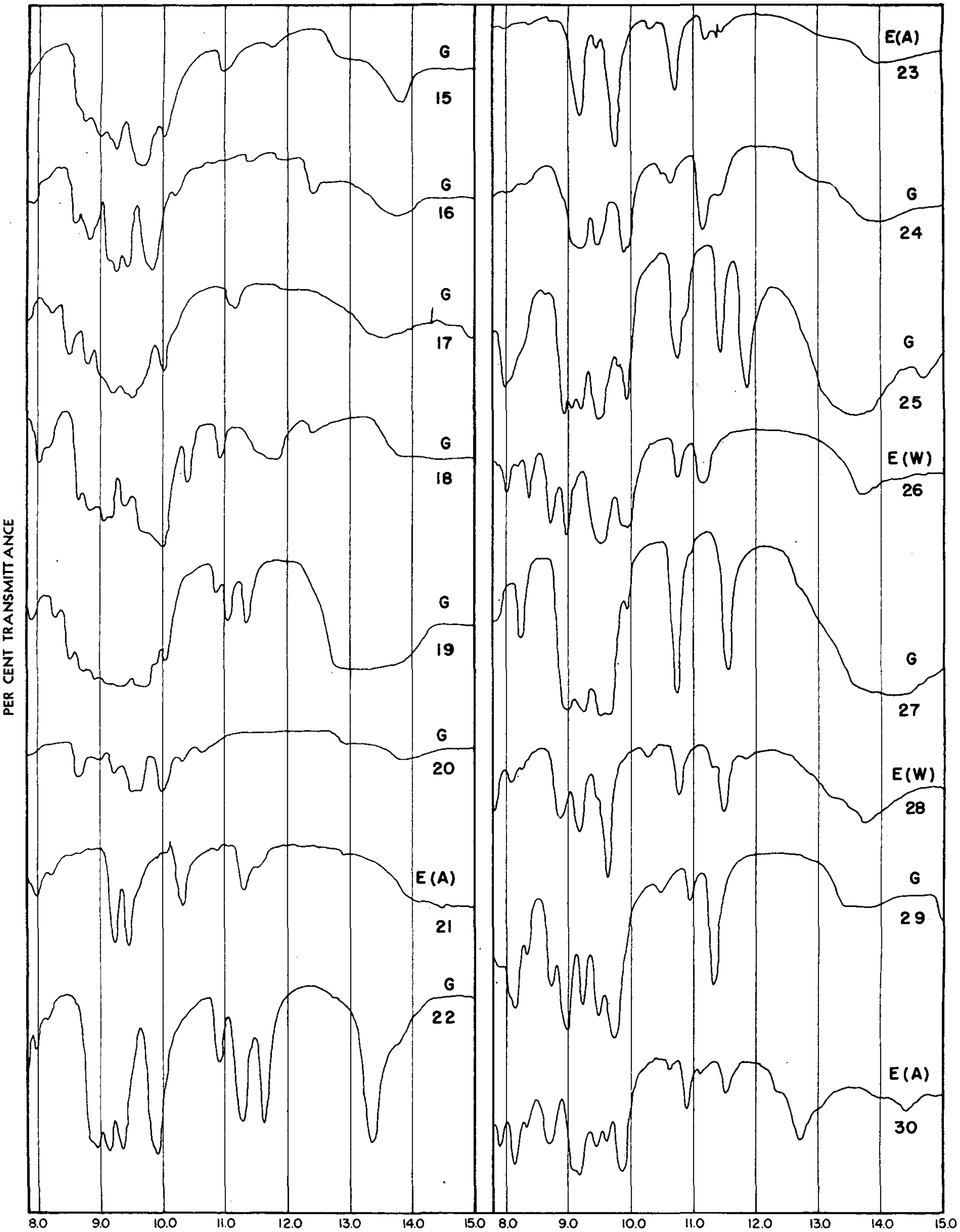

Figure 2. Infrared Spectra of Carbohydrates

15. Maltose
16. Mellibiose.H_2O
17. Cellobiose
18. Trehalose
19. D-Lactose
20. Raffinose
21. Erythritol
22. Xylitol
23. Mannitol
24. Sorbitol
25. Fucitol
26. *i*-Inositol
27. Dulcitol
28. Arabino-γ-lactone
29. Glucono-δ-lactone
30. Methyl (1-methyl-α-D-galacturonate)

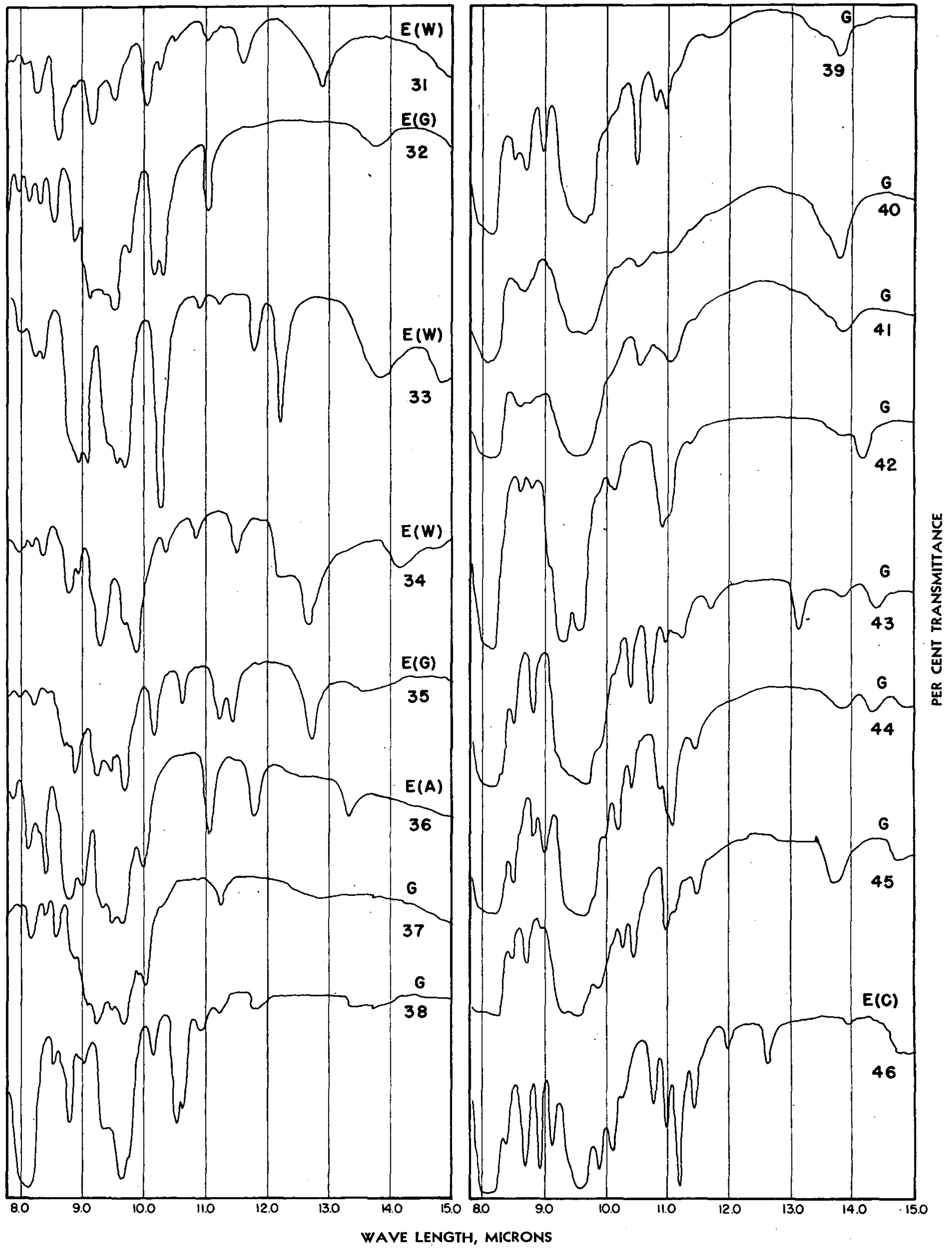

Figure 3. Infrared Spectra of Carbohydrates

31. D-Gluco-α-heptonolactone
32. Methyl β-D-xyloside
33. Methyl α-D-mannoside
34. Methyl α-D-galactoside.H_2O
35. Methyl β-D-galactoside
36. Methyl α-D-glucoside
37. Methyl β-D-glucoside
38. α-D-Glucose pentaacetate
39. α-Cellobiose octaacetate
40. α-Cellotriose hendecaacetate
41. α-Cellotetraose tetradecaacetate
42. β-D-Glucose pentaacetate
43. Methyl α-D-glucoside tetraacetate
44. Methyl β-D-glucoside tetraacetate
45. Methyl β-D-galactoside tetraacetate
46. Levoglucosan triacetate

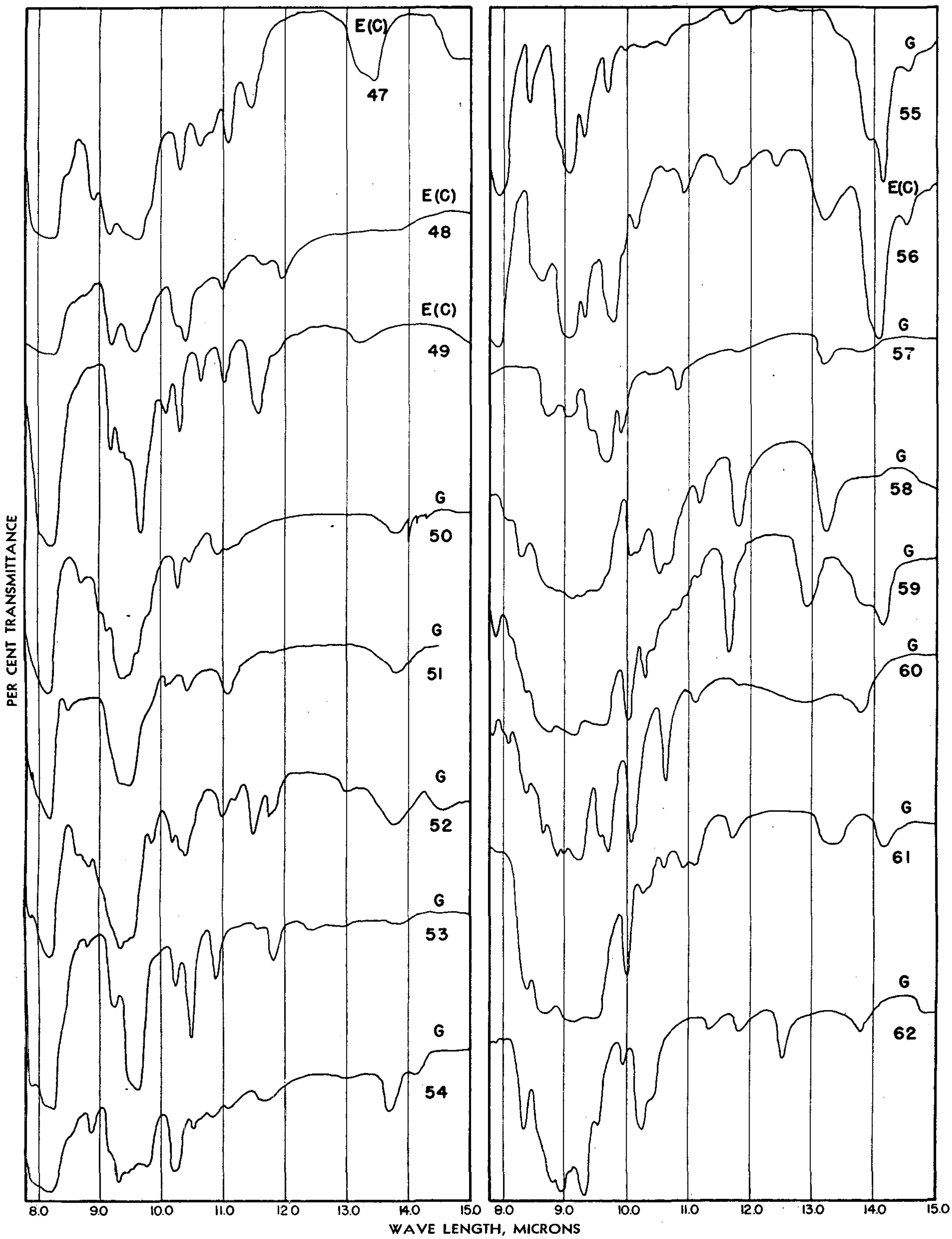

Figure 4. Infrared Spectra of Carbohydrates

47. α-L-Arabinose tetraacetate
48. Sorbitol hexaacetate
49. Mannitol hexaacetate
50. 3-Methyl D-glucose tetraacetate
51. Lactose octaacetate
52. D-Galactose dimethylacetal pentaacetate
53. D-Galactose diethylmercaptal pentaacetate
54. L-Rhamnose diethylmercaptal tetraacetate
55. D-Glucose diethylmercaptal pentabenzoate
56. 3-Methyl-D-glucose tetrabenzoate
57. 3-Methyl-D-glucose
58. 2,3,4,6-Tetramethyl-D-galactose
59. 2,3,4,6-Tetramethyl-D-glucose
60. 2,3,4,6-Tetramethyl-D-mannose
61. Methyl tetramethyl-D-glucoside
62. Methyl tetramethyl-α-D-mannoside

The oxidation of many sugars with periodate results in a cleavage of the carbon chain and the newly formed primary carbon atoms appear as aldehyde groups. Curve 5 is for the oxidation product of α-methylglucoside, which has the structure $CH_2OH—CH(CHO)—O—CHOCH_3(CHO)$ and it shows the band due to the C=O of the aldehyde group at about 6.2 microns. The nitrate bands show up very clearly in curve 6 at 5.9, 7.7, and 11.8 microns. The assignment of these bands to the various functional groups has been done empirically and is the result of the study of a large number of curves. The treatment of this subject by Barnes and co-workers (*1, 2*) has been extremely helpful.

Below about 8 microns all the structurally isomeric sugars show the same absorption bands; hence this portion of the spectrum has been omitted from the subsequent curves. The differences between these closely related compounds appear beyond 8 microns.

An examination of the curves shows that each compound has its own characteristic set of absorption bands and, except in one special case discussed below, no two curves are identical. In some cases the bands are not so strong and do not show up so clearly as might be desired. This is generally due to a large amount of scattering of the incident light by the crystals of the sample, which results in a lack of contrast between the light absorbed and that transmitted.

In the glycoside series the difference between the anomeric forms shows up very nicely. Thus the α-methylglucoside can be readily distinguished from the β-methylglucoside (curves 36 and 37), and in the methyl galactosides the alpha is again different from the beta compound (curves 34 and 35). In the series of esters there is an interesting group of compounds consisting of the acetates of α-glucose, α-cellobiose, α-cellotriose, and α-cellotetrose. In this polymeric homologous series (curves 38 to 41), the monomer, the dimer, and the trimer can be distinguished from each other. However, between the trimer and the tetramer there is very little difference, and between the tetramer and pentamer, which is not shown, there is no distinguishable difference. Apparently it is impossible to resolve the broad bands of the tri- and higher saccharides with the author's spectrometer, and any difference in detail which may exist between these spectra is invisible. The difference between the spectra of anomeric forms is again easily seen from a comparison of the curves for the alpha and beta forms of glucose pentaacetate (curves 38 and 42) and for the two forms of methyl glucoside tetraacetate (curves 43 and 44).

For mono- and disaccharides, and for their derivatives, infrared spectra may serve as a very useful tool in determining the presence of various functional groups for establishing the identity of a compound and determining the presence of impurities. It has the advantage over other physical measurements, such as melting point or optical rotation, that the spectrum is unique for each compound. Only a small sample is required, 15 mg., for evaporated films, and somewhat more for grinding in mineral oil, and the sample may be recovered. For this method to be useful for identification purposes it is necessary that the worker have at his disposal as complete a collection of curves of pure sugars as possible, and it was with this in mind that the accompanying curves were submitted for publication. The spectrum of any sugar is strongly influenced by the introduction of substituents. A comparison of the spectra of a series of derivatives of a given sugar reveals no band or arrangement of bands that is characteristic of the particular sugar. For this reason it has not been possible to identify a substituted sugar by a comparison of its spectrum with that of the corresponding unsubstituted sugar, nor does it seem likely that a polysaccharide can be identified by comparison of its spectrum with the spectra of the monosaccharides of which it is composed.

Curves 73 to 79 give the spectra of various cellulose derivatives. The bands in the short wave-length end of the spectrum characteristic of the various functional groups show up very well, but the bands in the region corresponding to the carbon-carbon and carbon-oxygen frequencies in the region of about 9 to 10 microns are very broad, as was the case with the tetrasaccharide discussed above. Curve 73 for nitrocellulose shows a weak oxygen-hydrogen band at 3 microns due to the fact that the cellulose is not completely nitrated, a carbon-hydrogen band at 3.45, and nitrate bands at 6.0, 7.8, 12, 13.3, and 14.3 microns. Cellulose was oxidized with nitrogen peroxide to polyglucuronic acid, which was then nitrated. Curve 74 shows the spectrum of this nitrated polyglucuronic acid which has the new band due to the C=O of the carboxyl group at 5.75 microns. A commercial sample of methylcellulose is shown in curve 75. It too shows a band at 5.7 microns, indicating the presence of carboxyl groups which must have been formed by oxidation of the cellulose in the manufacturing process. In the curve for cellulose-6-trityl ether the aromatic carbon-hydrogen band appears at 3.3 microns, and several bands due to benzene rings at 6.3, 6.65, and in the region of 13 and 14 microns can be seen.

To determine the possibility of using the infrared spectrum for the quantitative determination of a functional group—in this case the nitrate group—the curves for several different nitrocelluloses of known nitrate content were obtained.

Using the equation for Beer's law,

$$\log I_0/I = kcd \tag{1}$$

where I_0 and I are the intensities of the incident and transmitted light, respectively, k is the extinction coefficient, c is the concentration, and d is the thickness of the sample, an attempt was made to see if k is constant. Because c has been determined by an independent method, d can be measured, and $\log I_0/I$ can be obtained from the height of the absorption band, the equation can be solved for k. If k is known for a given absorption band, and has been found to be constant, then this value of k can be used for the analysis of an unknown and the equation solved for c.

To secure good accuracy the absorption band should be of such strength that 30 to 70% of the light is absorbed. The nitrate band at 6 microns is so strong that even for very thin films it showed almost complete absorption. The OH band at 3 microns is much weaker and more satisfactory for the purpose; furthermore, it has the advantage that for highly nitrated celluloses small differences in nitrate content are accompanied by relatively large differences in per cent of OH. Knowing the OH content, the nitrate content can be readily calculated. Films of such thickness as to give the OH band an absorption of about 50% were used. It was found that the value of k was not constant and one of the reasons for the lack of constancy is the difficulty of accurately measuring the film thickness, d, especially as the films are generally not of uniform thickness.

To circumvent this difficulty the ratio of the OH and CH bands was used. If the Beer's law equation for the OH band and for the CH band is written:

$$\frac{(\log I_0/I)_{\mathrm{OH}}}{(\log I_0/I)_{\mathrm{CH}}} = \frac{k_{\mathrm{OH}}c_{\mathrm{OH}}d}{k_{\mathrm{CH}}c_{\mathrm{CH}}d} \tag{2}$$

$$\frac{(\log I_0/I)_{\mathrm{OH}}}{(\log I_0/I)_{\mathrm{CH}}} = k^*c_{\mathrm{OH}} \text{ where } k^* = k_{\mathrm{OH}}/k_{\mathrm{CH}}\, c_{\mathrm{CH}} \tag{3}$$

and the equation for the OH band is divided by the equation for the CH band, a new Equation 2 is obtained in which the d's cancel, and which can be simplified to give Equation 3 if we assume that c_{CH} is independent of the nitrate content, which is probably not too bad an assumption, since the number of CH bonds per molecule is independent of the number of nitrate groups. The scattered radiation was corrected by taking as the value of I_0 not 100 but the per cent of light transmitted at a wave length at which the nitrocellulose has no absorption band—namely, 2.7 microns. The nitrocellulose films were made by evaporation of ethyl acetate solutions. To remove the solvent completely, the films were dried for 48 hours in a vacuum oven at 50° C.; however, the curves showed a strong band at 5.7 microns, indicating that solvent was still present. On soaking the films for several hours in

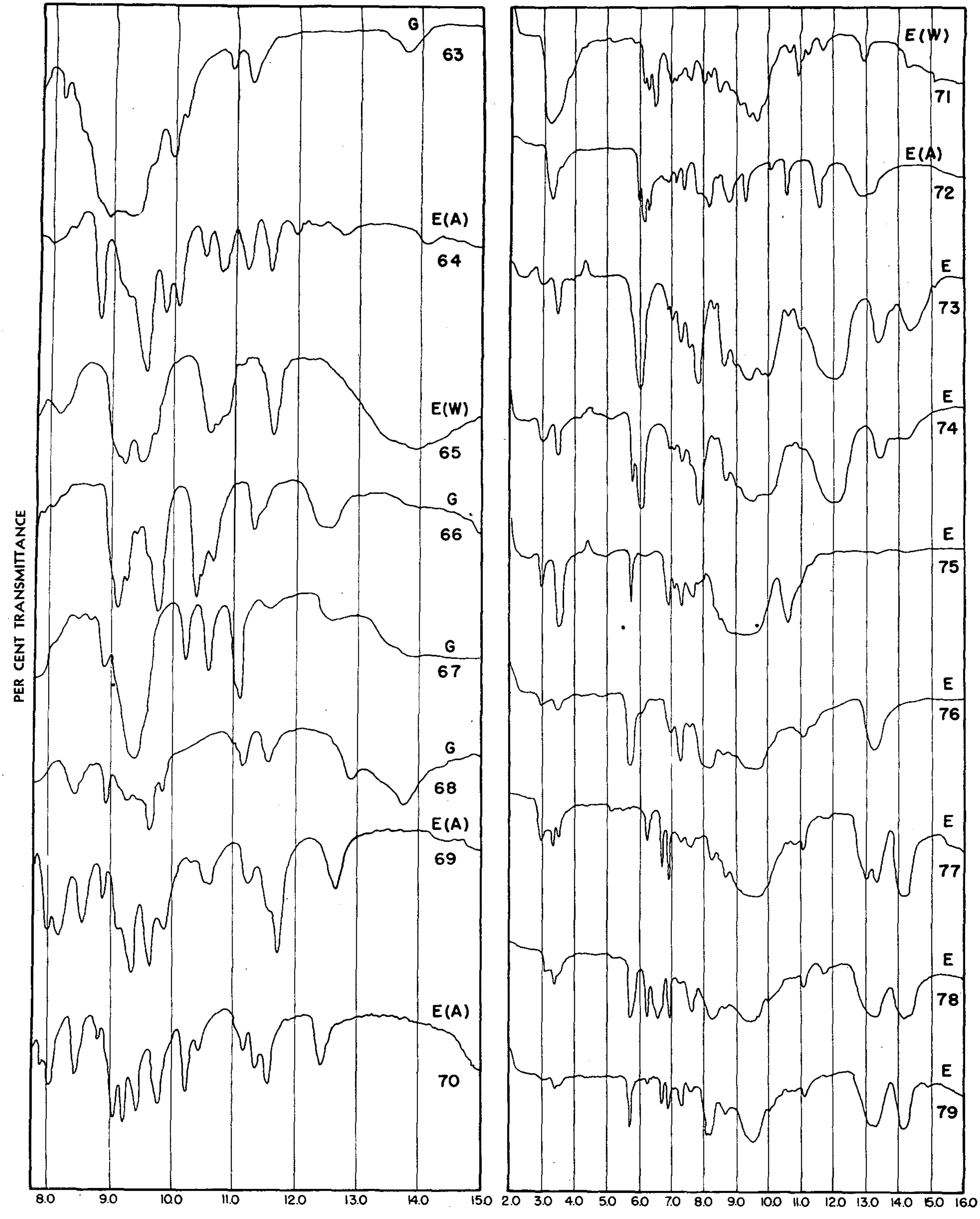

Figure 5. Infrared Spectra of Carbohydrates

63. Methyl 2,3,6-triethyl β-D-glucoside
64. Levoglucosan
65. D-Galactose oxime
66. D-Mannose oxime
67. L-Rhamnose diethylmercaptal
68. D-Galactose diethylmercaptal
69. 1,2,5,6-Diisopropylideneglucofuranose
70. 1,2-Isopropylideneglucofuranose
71. D-Glucosamine hydrochloride
72. Kojic acid
73. Nitrocellulose
74. Polyglucuronic acid nitrate
75. Methylcellulose
76. Cellulose acetate
77. 6-Trityl cellulose
78. 6-Trityl 2,3-bisphenylurethane cellulose
79. 6-Trityl cellulose acetate

Table II. Determination of Extinction Coefficient

Sample	% N	OH Groups per Glucose Unit	$(I_0/I)_{OH}$	$(I_0/I)_{CH}$	$\log (I_0/I)_{OH}$	$\log (I_0/I)_{CH}$	$\frac{\log (I_0/I)_{OH}}{\log (I_0/I)_{CH}}$	k^*
5	10.87	1.065	79/19.5	79/25	0.607	0.500	1.21	1.13
9	11.35	0.925	80.5/22	80.5/25.1	0.562	0.505	1.11	1.05
3	11.88	0.77	82/33	82/26	0.398	0.490	0.814	1.07
4	11.96	0.75	86/34.4	86/27.8	0.394	0.490	0.805	1.07
6	12.60	0.555	75/42.5	75/31.5	0.267	0.433	0.617	1.11
10	12.66	0.53	88/64.3	88/52	0.137	0.228	0.603	1.13
2	13.4	0.28	83/68	83/42.2	0.086	0.292	0.294	1.05
8	13.4	0.28	78.5/60	78.5/31.5	0.117	0.396	0.295	1.05

ether or in water and then drying again, the curves obtained no longer showed the carbonyl band. It is possible that the ether and the water are also retained by the film, but they are not readily detected from the infrared curves. Soaking the film in hexane and drying did not result in the removal of the ethyl acetate.

The results obtained from eight different samples are given in Table II. These films were soaked in ether. The variation in k^* which amounts to about 8% is probably due to the variation in the amount of solvent retained by the films. The nitrate group can be determined conveniently by chemical methods, but for groups which cannot be determined conveniently by chemical methods the spectroscopic method may be advantageous.

ACKNOWLEDGMENT

The author is indebted to Helen Johns for preparing the samples and operating the spectrometer, to M. L. Wolfrom, of Ohio State University, for supplying most of the sugar samples, and to E. I. du Pont de Nemours & Company for the nitrocellulose samples.

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Hysteresis Determinations with the Goodyear-Roelig Machine

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A description is given of a Roelig-type machine in which the test piece, under compression loading, was mechanically oscillated by means of a continuously adjustable eccentric weight rotated by a variable-speed motor. The hysteresis loop was traced by means of a light beam deflected by a system of optical levers in connection with a dynamometer. Photographic recording was advantageous for transient effects with single loops, although the equilibrium loops may also be traced on paper. The machine was found to be versatile for the selection of combinations of conditions such as frequency, force, and amplitude over its operating range. The effects of operational variables were investigated: frequency, duration of test, and static and dynamic load. The ratio of "static" to "dynamic" modulus depends more on amplitude than on frequency. Contrary to usual ideas, the static modulus actually may be greater than the dynamic modulus if the amplitude of the static deflection is sufficiently smaller than the dynamic amplitude. Data were secured for hysteresis determinations for synthetic polymers and Hevea compounds. Temperature rise during some of the tests was measured by means of a needle thermocouple to compare with hysteresis values from the loop. Tests on the same compounds were made by other methods of hysteresis evaluation. Determinations with the Goodyear Vibrotester, rebound pendulum, and flexometers were compared with results from the Roelig machine. Differences in the results could be reasonably interpreted on the basis of the different conditions of measurement and calculation. The importance of understanding the significance of a particular method of hysteresis determination for any specific application is thereby emphasized.

ROELIG (*8*) developed a machine for determining the hysteresis and dynamic modulus of rubber compounds to fill a need in the German program of synthetic rubber development which, in this country, was satisfied by a variety of generally less elaborate test methods (*2*). The broad purpose of these testing procedures is to furnish an evaluation of rubberlike performance under conditions of low strain amplitude and high rates of deformation, found in many important applications of rubber, such as tires. The Roelig machine represents a highly specialized German technical development and was not duplicated in this country during the war. At the conclusion of the war, interest in the machine led to the formulation of plans for securing several of them from Germany. These plans could not be consummated, but eventually a set of blueprints was secured, together with the dynamometer, which is the heart of the measuring system.

These blueprints were translated into the English system with a minimum of reworking to conform to machining practices in this country, and the machine was built in Akron. Provision was made for photographing the hysteresis loops in contrast to the German practice of manually tracing them on paper. Upon completion it was set up and put into satisfactory operation with little difficulty. The results secured seem comparable with those described by Roelig (*7*, *9*).

A Roelig machine has been reported as under procurement in Germany for use in the Rubber Research Laboratories at Croydon, England (*5*).

DESCRIPTION OF MACHINE

The Goodyear-Roelig machine is a rather large and strongly built apparatus. The mechanism, which itself weighs several

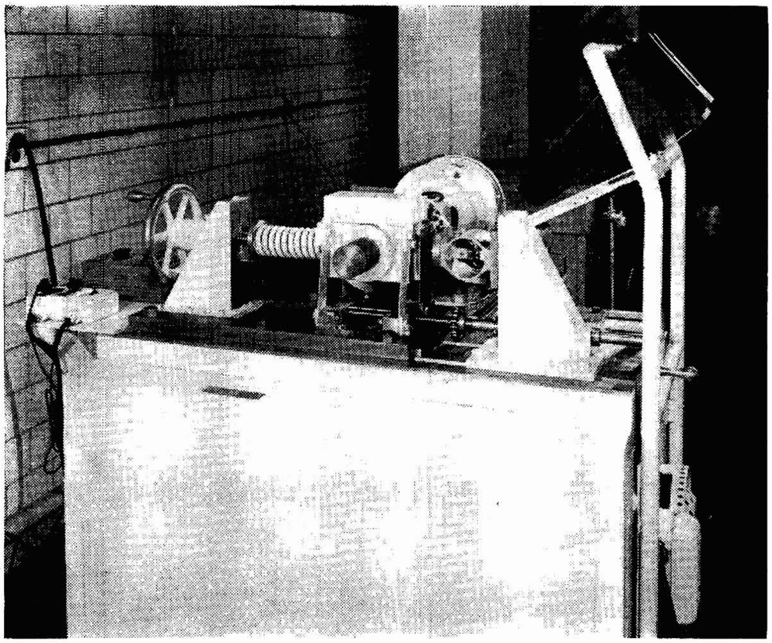

Figure 1. Goodyear-Roelig Machine

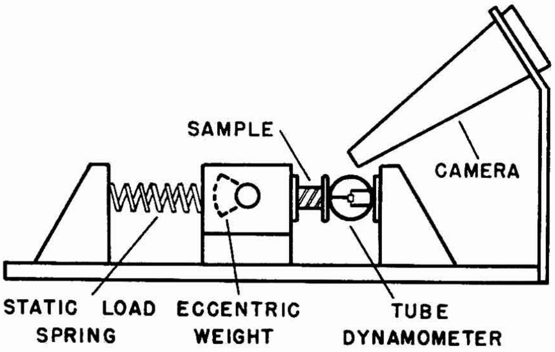

Figure 2. Schematic Drawing of Machine

hundred pounds, is mounted upon a concrete base weighing 2 tons. Any vibration of this massive base is isolated from the building floor by means of four short cylindrical rubber supports. A photograph of the machine is shown in Figure 1.

Explanation of the mechanism is facilitated by reference to Figure 2.

Vibration is produced by rotating an adjustable eccentric weight with a variable-speed direct current motor. Variation in the eccentricity of the rotating weight, which actually consists of two movable sectors, is permitted by an ingenious design involving the use of a spiral cam and screw arrangement. Adjustments may be made throughout the entire range with the machine either running or stationary.

Oscillation of the eccentric flywheel housing is constrained to a lateral motion by flexible cantilever mounting springs. At one end of this housing is placed the sample being tested, and at the other end is mounted a steel compression spring. As the housing vibrates, it compresses the test sample and spring alternately.

The periodic force thus applied to the sample is transferred through it to the tube dynamometer, which, in turn, is coupled to one of a system of rotating mirrors. The mirrors of this system act as optical levers to deflect a light beam in such a way as to produce an oscillographic trace upon a photographic film in the camera. The diagram of Figure 3 shows how this is accomplished.

Periodic compression of the dynamometer by the sinusoidally applied force rotates M_1 about its vertical axis to impart a horizontal component to the trace, while similar motion of the housing rotates M_3 about its horizontal axis to impart a vertical component to the trace. The vector addition of these two motions produces a resultant angular trace which assumes an approximately elliptical shape because of hysteresis of the sample.

The horizontal component of any point on the trace will, therefore, be proportional to the applied force at that instant; and the vertical component of the same point will be proportional to the displacement at that instant. A photograph of the optical system is shown in Figure 4. Part of the camera has been removed to expose the mirrors. The light source, a 2-watt zirconium oxide arc lamp, is not shown.

Operation of the machine and recording of data are comparatively simple. Before the sample is placed in position, a zero load vertical trace is photographed. This supplies a reference line, or base, from which static and dynamic loads may be measured. The sample, a cylinder 1.57 inches high and 1.57 inches in diameter, is next put in place; and with the motor stationary an initial static load is applied by compressing the static load spring. A second exposure of the film is made here to record this static load. The machine is then started and while running at some predetermined frequency, the flywheel is adjusted to produce the desired dynamic load. An exposure of the hysteresis loop may be made whenever desired.

An adjustment of the direction-changing mirror, M_2, permits the photographing of several loops on a single film.

Rotational velocity, or frequency, is measured stroboscopically. The normal frequency range is from 8.6 to 20 cycles per second. It has been found from experience that the most satisfactory operating frequency is at 12 or 15 cycles per second.

CALCULATIONS

Before explaining the method used in calculating results a short description of the hysteresis loop itself is necessary. Figure 5 shows the loop formed in tracing an essentially static compression-retraction curve. This curve was made by hand operation of the compression spring adjustment, allowing a time interval of 0.2 minute between successive points. The space between the first and second loops is due to creep. A similar loop made while the machine was running at a frequency of 12 cycles per second is shown in Figure 6. This dynamic hysteresis loop is differentiated from the static loop not only by the shorter period of the cycle but also by the nonuniform velocity during different parts of the cycle. The previously mentioned reference line, which is generated vertically at the machine, extends horizontally across the lower part of the figure.

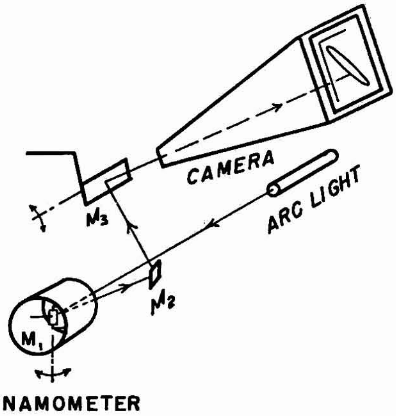

Figure 3. Diagram of Optical System

Dimensions L_S and L_D are proportional to the static and dynamic loads, respectively. C is proportional to the maximum deflection of the sample during vibration. It is twice the amplitude of oscillation. The area of the hysteresis loop, a, is proportional to the energy loss per cycle. Calibration of the machine shows that these dimensions on the film are equivalent to 303 pounds per inch for L and 0.0357 inch per inch for C. After the above dimensions have been carefully measured upon the film itself, or a copy enlarged to exactly double size, conversions to actual forces in pounds and deflections in inches are made.

The dynamic value of Young's modulus is calculated from the spring constant, which is the ratio of L_D to C as follows:

$$E = Q\frac{L_D}{C}$$

where E = dynamic modulus
L_D = dynamic load
C = dynamic deflection
Q = shape factor (sample height divided by cross-section area)

The per cent damping as defined by Roelig is

$$D = 100\,\frac{a}{A}$$

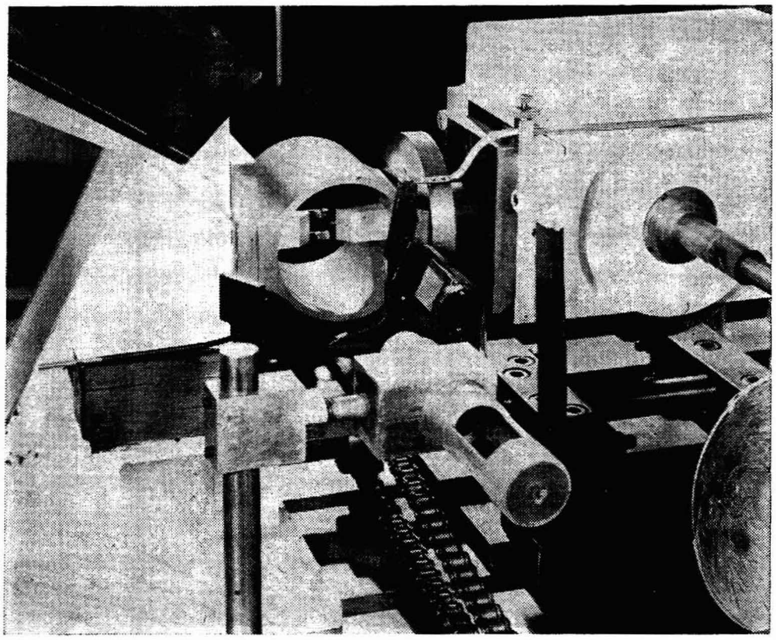

Figure 4. Optical System

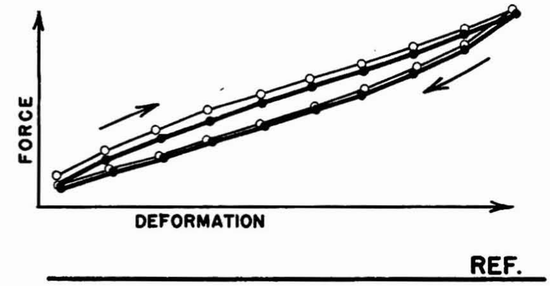

Figure 5. Static Type of Hysteresis Loop

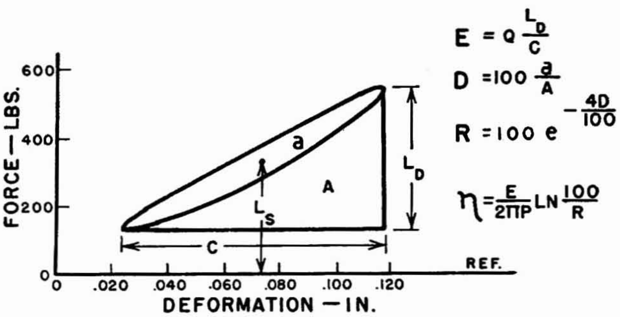

Figure 6. Calculations from Dimensions of Hysteresis Loop

where D = per cent damping
a = area of the hysteresis loop
A = area of triangle under loop

The formula used for calculating dynamic resilience is based upon equations developed from vibration theory (*4*). As used here, the term resilience is defined as the percentage of the vibrational energy which persists in the second of two successive free vibrations.

$$R = 100\,e^{-\frac{4D}{100}}$$

where R = per cent dynamic resilience
e = 2.718 . . .
D = per cent damping

Internal friction is calculated from the foregoing quantities using the equation

$$\eta = \frac{E}{2\pi p}\ln\frac{100}{R}.$$

where η = internal friction
E = dynamic modulus
p = angular frequency
R = resilience

A qualitative idea of the characteristics of a sample may be obtained by inspection of the loop itself—that is, a broad loop indicates higher energy loss than a narrow loop; a loop having a steep slope has a higher modulus than one of flat slope, etc. Loops from a variety of stocks are shown in Figure 7 to illustrate the range in shape and size which may be encountered.

COMPOUNDS USED

All compounds used are listed in Table I. Samples 1 through 12 are synthetic polymers in which conditions of polymerization were systematically varied. These polymers were prepared and furnished by the government laboratory together with the compounding formulas used with them. All illustrations used in discussing operational variables of the machine if not otherwise identified are copies of photographs of hysteresis loops from sample 2. Table II gives information on the polymers used. Samples 1 to 13, inclusive, were cured for 150 minutes at 292° F. Samples 14, 15, and 16 were cured for 100 minutes at 275° F. Sample 17 was cured for 30 minutes at 307° F.

EFFECT OF FREQUENCY

The effect of frequency of vibration on the dynamic modulus has been discussed by Stambaugh (*10*) for the range from 150 to

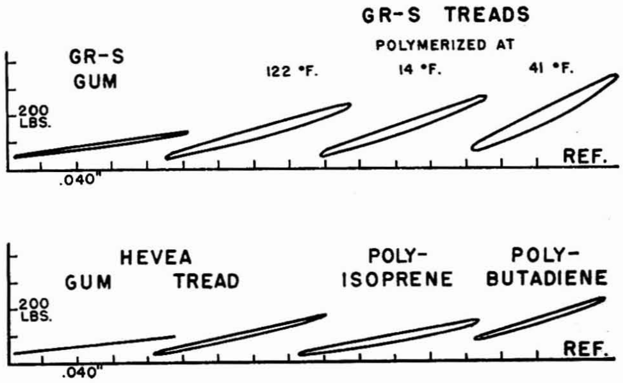

Figure 7. Typical Hysteresis Loops at 12 Cp.

Table I. Compounds Used

Sample No.	1 to 12 (except 2)	2	13	14	15	16	17
Polymer	100	100	100	100	100	100	100
EPC black	50	50	50	..	50	50	..
HMF black	..	..	..	..	..	..	50
Softener (BRT 7)	5	5	5	..	..	..	..
Zinc oxide	5	5	5	3	3	5	5
Sulfur	2	2	2.25	3	3	2	2
Captax	1.5	1.5	1	1	1	1.5	..
Stearic acid	..	1.5	3	4	4	2	3
25% diphenylguanidine master batch	..	0.8	..	..	..	..	..
Phenyl-2-napthylamine	..	..	..	1	1	1	..
Pine tar	..	..	..	3.75	3.75	..	..
Softener (Paraflux)	..	..	..	..	..	3	..
Tetramethyl thiuram disulfide	..	..	..	..	..	..	1

Samples 1 through 12 are of a special polymer series for which additional information is given in Table II. Samples 13, 14, and 15 are Hevea. Sample 16 is regular GR-S and sample 17 is GR-I.

Table II. Polymerization Data[a]

Sample No.	Polymer Type	Polymerization Temp., ° F.	Hydrocarbon Conversion, %	Raw Mooney Viscosity (212° F.)
1	GR-S	122	61	61
2	GR-S	41	60	60
3	GR-S	14	59	58
4	GR-S	122	42	54
5	GR-S	122	55	53
6	GR-S	122	72	48
7	GR-S	122	75	39
8	GR-S	122	100	43
9	GR-S	122	73	60
10	Polyisoprene	131	58	48
11	Polyisoprene	131	42	47
12	Polyisoprene	41	58	43

[a] Information supplied with polymers by government laboratory.

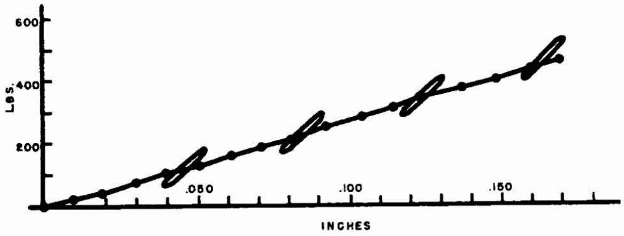

Figure 8. Relation of Dynamic Hysteresis Loops to Static Stress-Strain Curve

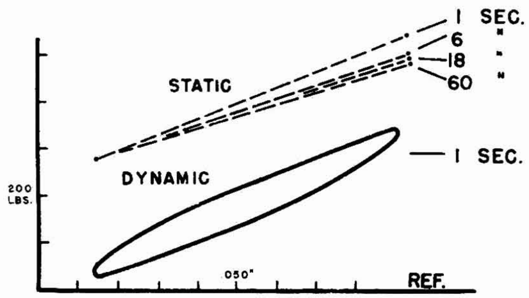

Figure 9. Comparison of Dynamic and Static Modulus

20 cycles per second. Using the Goodyear-Roelig machine this range has been extended downward to 8.6 cycles per second. By special manipulation frequencies of a fraction of a cycle per second may be obtained. In agreement with Stambaugh's work it was found that in normal operation there is very little dependence of modulus on frequency. However, essentially static measurements made with the Roelig machine and also with other apparatus show the static modulus to be lower than the dynamic modulus (*3*). To study this phenomenon several special tests were devised.

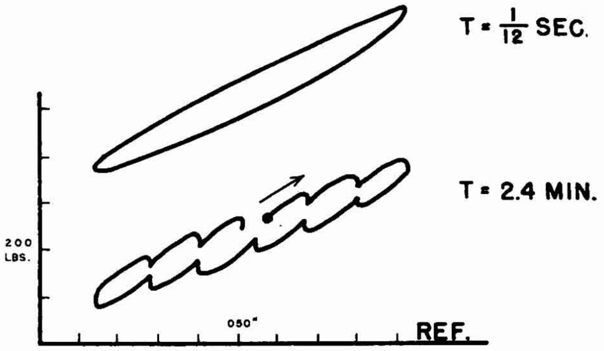

Figure 10. Flow during Periodically Interrupted Cycle

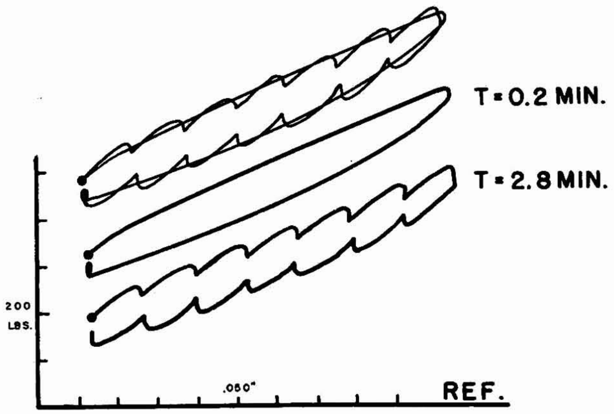

Figure 11. Comparison of Low Velocity and Interrupted Cycles

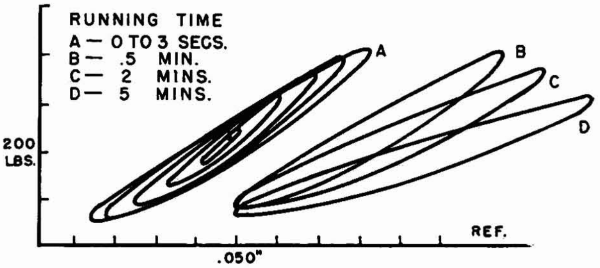

Figure 12. Change in Dynamic Properties during Test

Using the precompression spring adjustment, the load on a sample was periodically increased and instantaneous exposures of the film were made at intervals of 0.2 minute. Then, after returning to zero compression the path of this stress-strain curve was retraced, and several small amplitude dynamic loops were photographed. An enlarged copy of this film is shown in Figure 8. Points for the static condition have been connected to form a continuous curve. The dynamic modulus, as indicated by the steepness of the loops, is visibly greater than the static modulus.

A particular point on this static curve was chosen for further comparative tests as illustrated by Figure 9. A very short exposure, 0.01 second, was made of this point. Then the sample was quickly compressed about 0.090 inch and a second very short exposure made within 1 second. Without further compression, subsequent exposures were made after intervals of 6, 18, and 60 seconds. The decreasing height of these points indicates a definite decay of stress with time. A comparison with the slow speed dynamic loop below shows the 1-second static modulus to be very nearly equal to the dynamic modulus. Static moduli calculated for points of subsequent exposures are considerably lower.

Although from this it appears that the invariably higher dynamic modulus may be merely the result of an insufficient time interval for stress relaxation to take place, additional experiments, especially with different amplitudes, indicate that the phenomena are more complicated.

Further investigations of the effect were made using "interrupted cycles." This is the term used for the type of hysteresis loop shown below the normal loop in Figure 10. The procedure for obtaining such a loop was as follows:

> Beginning halfway through the compressive half of a cycle, quick compressive strokes of about 0.010-inch length were made. Less than a second elapsed during the motion. After each stroke, however, compression was halted for about 10 seconds. The downward movement of the trace during this halt is a definite indication of a decrease in stress, as may be expected from the results obtained in the static test of Figure 9. During the retraction half of the cycle just the opposite effect occurs. A sharp decrease in stress during the second of motion is followed by a slow rise in stress during the halt in deformation.

Results such as here shown are illustrative of the phenomena known as "delayed elasticity," "time effect," etc. They offer another approach to a problem which is receiving the attention of workers in the field of fibers (*6*) as well as rubber (*1*).

An interesting comparison of such an interrupted cycle to a very slow speed dynamic loop is shown in Figure 11. The loops are shown separately and also in a superimposed position. This shows that the dynamic loop represents an average of the extremes in stress of the interrupted cycle.

EFFECT OF DURATION OF TEST

The method of obtaining data by means of a photograph of the hysteresis loop makes the machine particularly useful in studying the effect of the duration, or running time, of the test. Pictures may be made at intervals throughout the test and studied later. Figure 12 illustrates this point. What appears to be a series of concentric loops at the left of the figure is actually the trace formed as the machine starts from rest and comes up to normal speed. The group of three loops to the right shows how the modulus and damping gradually decrease as time passes.

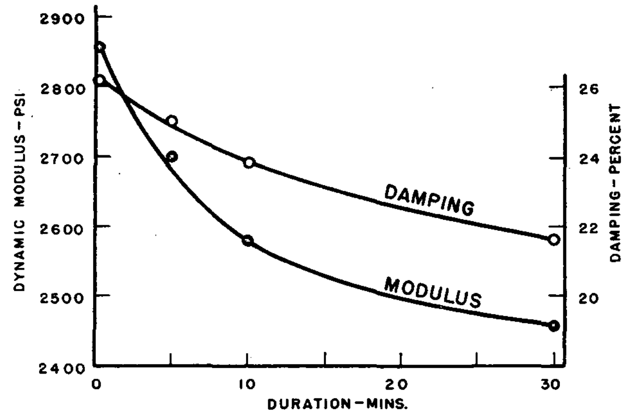

Figure 13. Change in Dynamic Properties during Test

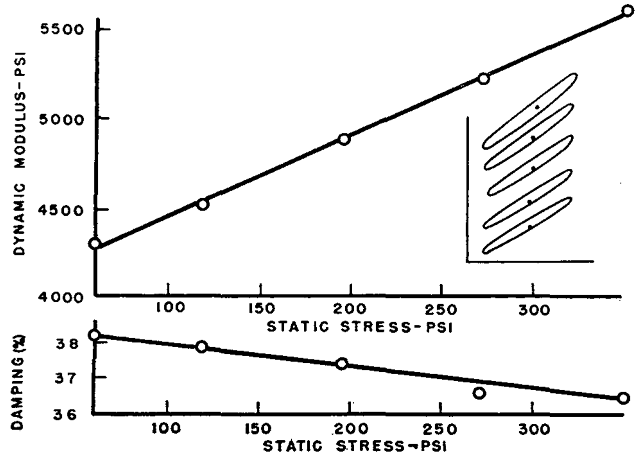

Figure 14. Effect of Increasing Static Stress

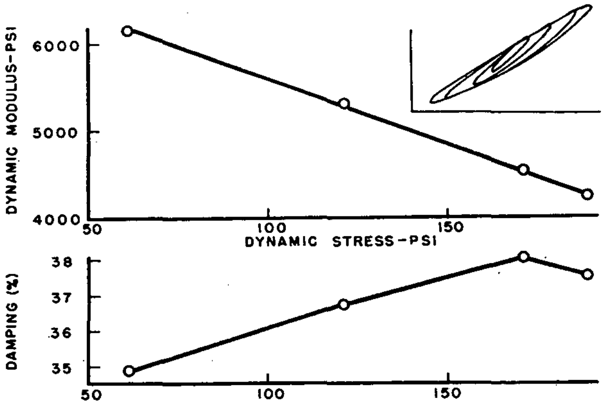

Figure 15. Effect of Increasing Dynamic Stress

Data from a similar series of loops have been plotted to form the curves of Figure 13. Values of both modulus and damping are highest during the first few minutes of the test but decrease rapidly and approach equilibrium conditions after 10 to 20 minutes. Although some of this change is undoubtedly due to temperature increase in the sample, a considerable part is probably due to orientation or structural viscosity, a phenomenon similar in an extreme example to the thixotropic effect found in gels.

Aside from such information of theoretical interest as may be obtained from study of this type of test, there is the practical consideration of the question of how long to run samples in routine testing. In the interest of economy of time it is desirable to vibrate each sample only as long as necessary to get reliable results. Data from a number of such tests indicate that a running time of 10 minutes gives consistent results.

EFFECT OF STATIC LOAD

The static load, or preload, applied to the sample may be varied over a wide range. In testing a stiff compound the static stress may be made as high as several hundred pounds per square inch without unduly distorting the sample. Results of a test in which the static load was systematically increased while the dynamic load was held constant are shown in Figure 14. Modulus is affected much more than damping for this sample.

EFFECT OF DYNAMIC LOAD

An increase of the dynamic load produces an effect on modulus which is just opposite that obtained by increasing the static load. This is shown in Figure 15. The decrease in modulus is characteristic of loaded stocks. The increase in damping shown by this sample does not occur in all compounds. Damping, which is a function of both internal friction and modulus, may either increase or decrease, depending on the rates of change of these quantities.

The decrease in modulus with increase in dynamic stress, and consequent increase in amplitude, has been observed by other workers (*3, 10*). Dynamic stress seems to have a more pronounced effect than does frequency. Evidence of this is shown in Figure 16. The small loop was traced while the sample was being deformed at a linear velocity of approximately 0.4 inch per minute, as compared to the large loop which was traced while the same sample was being deformed at an average rate of over 100 inches per minute. For the dynamic loop, of course, the velocity is not uniform. Because of the large difference in amplitude the static modulus is actually greater than the dynamic modulus, which is just the reverse of usual observations. The sample was at its equilibrium running temperature when these loops were photographed.

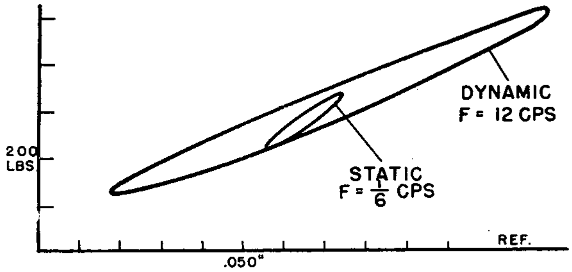

Figure 16. Effect of Amplitude and Frequency

The effect of dynamic stress, or amplitude of oscillation, which may include structural effects due to orientation viscosity must be considered along with the "delayed elasticity" effect in forming any theories to explain the difference between dynamic and static moduli.

HEAT GENERATION

One of the most important applications for hysteresis determinations is to enable an estimation of the temperature rise of a compound under various circumstances of use.

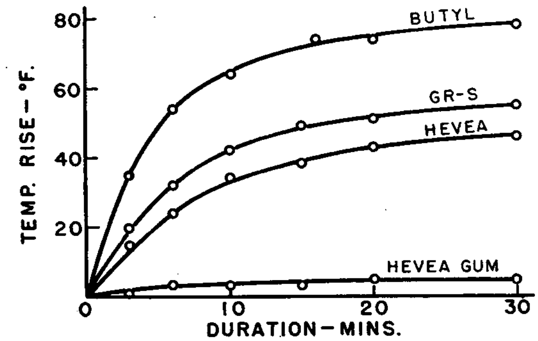

Figure 17. Temperature Rise in Tread Stocks during Test

Temperature rise in the sample in the Roelig machine may be easily measured while the test is in progress by inserting a needle-type thermocouple. In Figure 17 are shown curves giving the temperature rise during tests of four compounds. The increase in heat generation brought about by the addition of carbon black is evident in the two curves for Hevea, where the only difference between the two compounds is the addition of 50 parts of EPC black to one. The butyl compound, which has very low resilience, shows the largest temperature increase.

This type of curve has been thoroughly discussed by Springer (*9*).

Because of the difficulties and uncertainties in calculating the values of quantities to be used in Springer's equation, a relation for relative heat generation based upon theoretical considerations and measurements of the hysteresis loops may be used instead. Two expressions are used, depending upon whether the samples are vibrated at constant dynamic stress or constant dynamic amplitude. For the former the expression is

$$H_f \propto \frac{(100 - R)\,F^2}{E}$$

For the latter it is

$$H_x \propto (100 - R)EX^2$$

where H = relative heat generation
R = dynamic resilience
E = dynamic modulus
F = dynamic stress
X = amplitude

For purposes of comparison, a sample of Hevea tread stock having a modulus of 948 pounds per square inch and a resilience of 41.8% was arbitrarily assigned a heat generation value of 100 units. Other samples were then compared to this standard.

Table III lists the results of such calculations for the group of special synthetic stocks and one natural rubber compound for both the Roelig machine and the Vibrotester (*4*). In the same table are also shown temperature rises measured during standard flexometer tests. Calculated relative values of heat generation have been plotted against actual measurements of temperature rise in Figure 18. Temperature readings were made using the needle thermocouple at the time the hysteresis loop was photographed. Thus data from the hysteresis loops may be used with

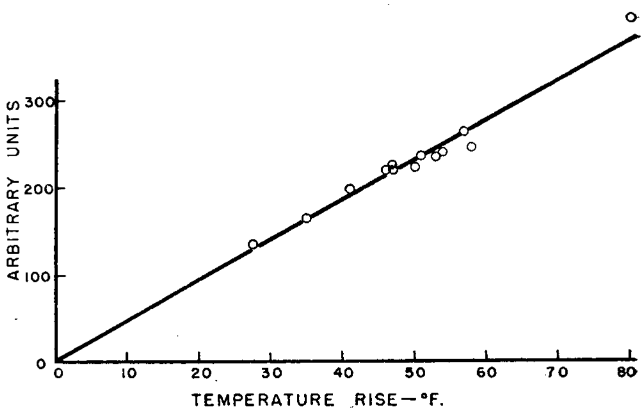

Figure 18. Calculated Heat Generation *vs.* Measured Temperature Rise

Table III. Heat Generation

Sample No.	Calculated Relative Heat Generation, H_x		Measured Temperature Rise, Flexometer, ° F.	
	Roelig	Vibrotester	Goodyear	Goodrich
1	224	224	141	55
2	396	..	..	63
3	266	302	135	47
4	242	260	135	55
5	238	254	145	56
6	221	249	137	56
7	229	254	135	57
8	247	298	158	..
9	236	258	147	60
10	168	196	121	56
11	221	233	153	60
12	200	219	125	54
13	137	192	100	40
Standard	100	100		

Table IV. Dynamic Modulus

Sample No.	Roelig, Lb./Square Inch		Vibrotester, Lb./Square Inch	Pendulum Rebound, Inch Indentation
	Constant stress	Constant amplitude		
1	2690	1830	2030	0.193
2	9240	2980	..	0.143
3	3540	2360	2495	0.179
4	2880	2010	2155	0.188
5	2930	1940	2020	0.187
6	2110	1845	1915	0.193
7	2800	1830	1960	0.193
8	2490	1780	2200	0.184
9	2660	1960	2015	0.191
10	1255	1270	1445	0.222
11	1650	1520	1665	0.204
12	1900	1725	1780	0.210
13	1730	1600	1715	0.229

Table V. Dynamic Resilience

Sample No.	Roelig, % Constant stress	Roelig, % Constant amplitude	Vibrotester, %	Pendulum Rebound, % Rebound resilience	Pendulum Rebound, % Dynamic resilience
1	33.6	32.6	33.6	54.5	29.8
2	33.4	26.6	..	43.3	18.8
3	40.6	37.6	33.2	54.0	29.2
4	36.8	33.7	33.3	55.5	30.9
5	32.6	32.4	30.4	54.5	29.8
6	32.8	33.8	28.1	54.0	29.2
7	26.9	30.9	28.6	53.5	28.7
8	23.8	23.2	25.1	48.3	23.3
9	31.7	33.4	29.3	53.0	28.1
10	28.8	26.9	25.0	48.7	23.8
11	21.3	19.7	22.5	46.5	21.6
12	34.6	36.0	32.0	56.0	31.4
13	52.1	53.0	38.2	62.5	39.1

Table VI. Internal Friction

Sample No.	Vibrotester, Kilopoises	Roelig, Kilopoises
1	62.7	300
2	..	575
3	77.8	334
4	66.9	317
5	68.0	318
6	68.3	291
7	71.1	313
8	85.8	378
9	69.5	312
10	56.6	243
11	69.6	358
12	57.0	255
13	46.7	149

good precision to estimate the relative heat generation of compounds in particular applications.

CORRELATION OF TESTS

Although each of the many types of hysteresis testing machines has unique characteristics which may make it most suitable for use in obtaining particular information, it is of interest, where possible, to compare similar quantities measured by them. This has been done for the Roelig machine, Vibrotester, and rebound pendulum with the results listed in Tables IV, V, and VI.

All tests with the Roelig machine were made using a static compression of 9.6%. Constant amplitude tests were run at an amplitude of ±3.2%. Constant dynamic load tests were run under load of ±41 pounds per square inch. All tests with the Vibrotester were run under static compression of 8%. A constant amplitude of ±2.1% was maintained. Vibration frequencies were 12 cycles per second for the Roelig machine and 60 cycles per second for the Vibrotester. Pendulum rebound tests were made using standard procedure.

Agreement between Roelig and Vibrotester results is good for modulus when amplitude effects are taken into consideration. Narrow loops obtained for high resilience stocks such as sample 13 are difficult to measure and consequently increase the error in resilience values. Certain differences in the methods of expressing results must be considered in comparing rebound values. Although no exact modulus is calculated for rebound tests, the generally used concept—that a smaller indentation indicates a higher modulus—may be used to get qualitative comparisons. Resilience as determined with a rebound test must be converted to a complete cycle basis before comparing it to resilience values from the dynamic testers. This is done by squaring the original result. When this is done, good agreement is obtained.

Internal friction may be calculated for both Roelig and Vibrotester tests, but is not usually found for rebound tests. The differences shown in the table are due principally to the difference in frequency. Internal friction varies inversely with frequency to a close approximation.

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Acid-Base Determinations of Petroleum Products

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Extensive data are presented to show that single-phase rather than two-phase equilibrium titration for determining the acidic and basic characteristics of petroleum products is preferable.

FOR years the determination of acidic and basic compounds in petroleum products has been a difficult analytical problem. Originally, the determination was made to measure the effectiveness of treating processes for removing the strong acids and bases used in refining. Later it became of value for determining acidic oxidation products formed during usage and addition agents of either acid or basic character. Hence the analyst is now confronted with the acid-base titration of nonaqueous solutions which may contain organic or inorganic acids or bases, esters, lactones, phenols, soaps, resins, etc.

The conventional analytical method has been extraction, without actual segregation of the layers, from the petroleum to an aqueous or alcohol layer and titration of the acid or base in the separated layer (*1, 3*). Because of the poor reproducibility of this method, Committee D-2 on Petroleum Products of the American Society for Testing Materials has carried out an extensive co-

Table I. Acid and Base Numbers of Test Oils by A.S.T.M. D 663–46T

Sample	Laboratory A: Acid Number, Mg. of KOH per Gram[a] Analyst A	Analyst B	Analyst C	Analyst D	Maximum Deviation Single operator	Maximum Deviation All operators	Acid Number Laboratory B	Acid Number Laboratory C
S-83 (Used)	1.30, 1.19	1.33, 1.62, 1.10	0.90, 0.98	1.40, 1.70	0.52	0.80	1.51, 1.57	2.39, 1.48
S-84 (Used)	0.91	0.73, 0.63	0.97, 0.77	1.08, 0.94	0.20	0.45	0.81, 0.87	1.59, 1.25
S-85 (Used)	1.04	1.45, 1.34	0.81, 0.80	1.17, 1.08	0.11	0.65	3.60, 3.65	1.43, 1.14
S-86 (New)	−0.30	0.06, 0.05	0.00	0.05	..	0.36	−0.18, −0.18	0.057, 0.057
S-87 (Used)	1.16	1.46	0.98, 1.16	2.52, 2.85	0.33	1.87	2.10, 2.38	2.57, 1.19
S-88 (New)	−0.37	−0.39	−0.22	0.05	..	0.44	−0.30, −0.36	0.057, 0.03
S-89 (Used)	0.79	1.23, 1.08	0.89, 1.55	2.87, 3.02	0.66	2.23	2.20, 2.26	2.68, 1.54
S-90 (New)	−0.29	−0.54	−0.25	−0.46, −0.44	..	0.25	−0.24, −0.30	0.057, 0.057
S-91 (Used)	1.43, 1.16	0.98	0.98, 0.89	1.29, 1.32	0.27	0.54	1.22, 1.33	1.48, 1.15
S-92 (New)	0.13	0.36, 0.08, 0.14	0.00	0.06	..	0.42	−0.12, −0.18	0.029, 0.057
S-93 (Used)	0.42, 0.46	0.98	0.63, 0.53	0.88, 1.35	0.47	0.93	1.28, 1.33	1.37, 0.85
S-94 (New)	−0.47	−1.40	−0.46	−1.45	..	0.99	−0.66, −0.66	−0.17, −0.22
S-95 (Used)	0.56	1.24, 0.85, 0.53	0.87, 0.71	1.24, 1.26	0.71	0.73	1.45, 1.33	1.48, 1.19
S-96 (New)	−0.10	−0.10	−0.09	−0.06	..	0.04	−0.18, −0.18	0.057, 0.057
S-97 (Used)	0.65	0.99	0.77, 0.71	1.38	..	0.73	1.15, 1.39	2.45, 1.08
S-98 (New)	0.04	−0.06, −0.05	0.03	0.05	..	0.11	0.06, 0.06	0.57, 0.11
S-99 (Used)	1.84	2.97	1.39, 1.40	3.52	..	2.13	3.25, 3.36	3.36, 2.16
S-100 (Used)	1.16	0.75	0.77, 0.69	1.41	..	0.72	1.33, 1.33	1.08, 0.79
S-101 (New)	−0.46, −0.50	−0.54, −0.46	0.36	0.52	0.08	0.16	−0.35, −0.35	−0.057, −0.11
S-102 (Used)	0.43	0.40	0.38, 0.46	0.58	..	0.20	0.58, 0.52	1.03, 0.85
S-103 (New)	0.29, 0.30	0.19	0.21, 0.16	0.44	0.05	0.25	0.46, 0.46	0.11, 0.31
S-104 (Used)	1.02	1.30, 1.73, 1.56	0.50, 0.85	1.96	0.43	1.46	1.33, 1.45	0.86, 1.53
S-105 (New)	−0.15	−0.27	−0.20, −0.23	−0.24	..	0.12	−0.18, −0.18	0.11, 0.11
S-106 (Used)	1.47	3.26	1.52, 1.40	4.31	..	2.84	3.94, 4.17	2.31, 5.00
S-107 (New)	−0.38	−0.78, −0.87	−0.30, −0.29	−0.72	0.09	0.58	−0.54, −0.54	−0.23, −0.14
S-108 (Used)	1.05	1.18	0.54, 0.59	1.22	..	0.68	−0.72, −0 78	0.86, 2.51
S-109 (New)	−0.34	−1.16	−0.24, −0.22	−0.31	..	0.94	−1.74, −1.57	−0.057, −0.23
S-110 (Used)	0.48, 0.52, 0.68	0.81, 0.71	0.44, 0.47	0.47	0.20	0.37	0.70, 0.81	0.68, 0.68
S-111 (New)	−0.13	−0.15	−0.11, −0.11	0.05	..	0.20	−0.30, −0.24	0.17, 0.03
S-112 (Used)	0.64, 0.59	1.02	0.49, 0.47	0.64	..	0.55	0.75, 0.81	0.97, 1.14
S-113 (New)	−0.44	−0.54, −0.43	−0.23, −0.31	−0.25	0.09	0.31	−0.54, −0.54	−0.17, −0.57
S-114 (Used)	0.92, 0.99	1.39	0.62, 0.70	0.88	0.08	0.77	1.45, 1.39	1.42, 0.91
S-115 (New)	0.10	0.12	0.00, 0.00	0.15	..	0.15	0.06, 0.06	0.11, 0.17
S-116 (Used)	1.90, 2.11	0.99, 1.71, 2.67	1.07, 1.22	2.34	1.68	1.68	1.97, 1.91	3.08, 2.90
S-117 (New)	−0.41	−0.72	−0.35, −0.22	−0.31	..	0.50	−0.60, −0.60	−0.11, −0.057
S-118 (Used)	0.89, 0.94	1.37	0.84, 0.95	0.84	0.11	0.53	1.51, 1.51	2.39, 2.45
S-119 (New)	−0.29, −0.33	−0.43, −0.35	−0.33, −0.31	−0.31	0.08	0.14	−0.48, −0.42	−0.11, −0.23
S-120 (Used)	1.38, 1.83, 1.71	2.06	1.43, 1.28	1.78	0.33	0.78	2.26, 2.20	1.59, 1.23
S-121 (New)	−0.44, −0.50, −0.37	−0.67	−0.82, −0.54	−0.33	0.28	0.49	−0.78, −0.78	−0.17, −0.23
S-122 (Used)	2.53	0.95, 1.05	1.81, 2.49	2.60	0.68	1.65	2.20, 2.30	2.11, 4.65
S-123 (New)	0.25	0.44	0.54, 0.73	0.26	..	0.48	0.70, 0.87	0.63, 0.91
S-124 (Used)	2.67	2.82	2.36, 3.74	0.81	..	2.93	4.58, 4.58	2.79, 5.07

[a] Minus sign indicates base number.

operative program with the object of improving the methods for the determination of acids and bases in petroleum products. This work, summarized in this paper, included attempts to standardize the many variables in the two-phase extraction method, and a study of single-phase titration methods.

As a result of the studies described here, it was concluded that none of the two-phase equilibrium procedures could be controlled to give reproducible results. Because an excellent single-phase electrometric method (*4*) had been developed and standardized (*3*, *5*), cooperative work was carried out in the titration of single-phase solutions, using color indicators to determine end points. Two methods were found which gave reproducible results. One of these, a solution in benzene-isopropyl alcohol using α-naphtholbenzein indicator, was selected for A.S.T.M. standardization, inasmuch as the results were in good agreement with those obtained by electrometric titration.

TWO-PHASE METHODS

Because it was recognized that a number of variables could affect the results of a two-phase equilibrium titration, an editorial group spent several days rewriting A.S.T.M. Method D 663–44T (*2*). Every effort was made to use the most exact and rigid wording, so that temperature, time, and agitation would be reproducible between laboratories. The resultant procedure, D 663–46T (*3*), was then tested on a group of forty-two oils by three laboratories, using one to four analysts in each laboratory. All these men had considerable experience on conventional acid-base determinations, and a number of them had long experience on the titration of used petroleum lubricants.

Table I shows the results of this work. The average results varied tremendously between laboratories, and differences of 50 to 60% were obtained in the same laboratory.

It is interesting to note the experience of laboratory A. When the method was first received, each analyst was requested to study it carefully, and then to carry out the acid-base determinations on the test series of used oils. The results shown in Table I are those obtained on this first attempt.

Because the results were not satisfactory, a conference of the

Table II. Acid and Base Numbers of Selected Test Oils

(By A.S.T.M. D 663–46T. Four analysts after discussion of procedure[a])

Sample	Acid Number, Mg. of KOH per Gram Analyst A	Analyst B	Analyst C	Analyst D	Maximum Deviation Single operator	Maximum Deviation All operators
S-83 (Used)	1.12 0.95	1.18 1.03 1.11	1.02 0.70	1.14 1.13 1.19	0.32	0.49
S-85 (Used)	0.88 0.83	1.14 1.23	0.80 0.64	1.01 1.07	0.16	0.43
S-87 (Used)	2.58 2.63	1.98 2.07	1.15 0.91	0.95 1.04	0.24	1.72
S-88 (New)	−0.22 −0.24	−0.29 −0.37 −0.38	−0.17 −0.22	−0.67 −0.61 −0.62	0.09	0.50
S-89 (Used)	4.46 3.78	2.17 2.58	0.93 0.96	2.29 2.33	0.68	3.53
S-91 (Used)	1.90 1.80	1.35 1.18 1.32	0.91 0.97	1.72 1.72	0.17	0.99
S-99 (Used)	2.02 1.82	1.76 1.77	1.91 1.98	1.80 1.77 1.98	0.21	0.26
S-107 (New)	−0.22 −0.24	−0.48 −0.47	−0.22 −0.27	−0.72 −0.75	0.05	0.53
S-109 (New)	−0.22 −0.24	−0.33 −0.37	−0.21 −0.14	−0.86 −0.89	0.07	0.75
S-116 (Used)	1.48 1.48	1.10 0.95 1.10	0.64 1.01	1.99 2.30	0.37	1.66
S-122 (Used)	2.36 2.85 2.49	2.19 2.29	1.48 1.11	3.67 3.22	0.49	2.56
S-124 (Used)	1.80 1.72	2.94 2.58	2.13 1.96	3.72 3.21	0.51	2.00

[a] A made an average of 4 determinations to get successful results reported, B made 4, C made 2, and D made 3.

Table III. Results on One Sample, Varying Mixing or Heating Period

Sample Swirled during Heating Period	Usual Titration, Both Phases Present	Titration of Aqueous Phase after Separation
Continuously	1.67, 1.93	0.66, 0.64
Last half	1.37, 1.49	0.54, 0.54
Not swirled	1.03, 0.75	0.44, 0.46
Continuously, followed by 3-min. shaking in separatory funnel	2.82, 2.56	2.02, 2.10
5-min. shaking in separatory funnel	3.25, 3.65	2.40, 2.36
Not swirled during heating (100-sec. titration time with swirling)	1.70	...
Not swirled during heating (74-sec. titration time with swirling)	0.96	...
D 664-46T (electrometric)	7.0	...

Table IV Comparison of Neutralization Number Methods

		Sample Numbers														
Method	Laboratory	S 148	S 149	S 150	S 151	S 152	S 153	S 154	A	B	C	D	B1	205-72	215-72	228-72
A.S.T.M. D 664-46T, electrometric	A	1.3	3.0	5.0	7.0	7.0	3.9	3.9	3.3	2.1	3.9	1.7	0.0	6.2	6.1	2.1
	B	2.1	4.4	5.0	7.7	7.4	..	..	3.8	2.3	4.5	2.7	0.0	6.3	5.5	3.2
	C	1.5	3.4	4.8	6.1	6.6	..	..	3.2	1.9	3.5	1.9	0.1	6.0	4.4	2.2
α-Naphtholbenzein	A	1.7	2.6	4.9	6.0	5.5	3.9	3.8	3.6	2.5	4.4	3.6	0.2	6.1	4.8	2.0
	C	1.7	2.8	4.6	5.5	5.4	..	..	3.0	1.9	3.2	2.1	0.2	4.9	6.2	1.9
Alkali blue	A	1.2	2.5	3.7	4.9	5.0	3.9	4.0	2.5	1.8	2.7	1.5	0.1^a	4.3	3.1	1.5
	B	1.6	3.0	4.4	5.9	6.0	..	..	4.2	3.1	4.7	3.7	0.1	5.1	4.6	3.1
	C	1.8	3.3	4.6	6.2	4.8	..	..	2.9	2.1	3.5	2.1	0.2	5.1	4.2	2.1
A.S.T.M. D 663-46T	A	0.5	0.9	1.6	1.3	1.1	2.9	2.3	1.5	0.6	1.3	0.6	0.0^a	1.6	0.9	0.4
A.S.T.M. D 663-46T, butyl Cellosolve	A	0.7	2.1	3.1	3.1	3.2	3.6	3.4	..	..	..	..	..	..	..	..
Naphtha-alcohol	A	1.8	2.4	3.4	4.8	4.8	3.9	4.0	3.9	3.0	4.6	2.7	0.3	5.8	5.8	2.8
Whiting method	A	2.0	3.5	5.3	6.0	6.6	4.3	4.4	3.6	2.8	4.4	2.6	0.3	6.4	5.3	2.8
	B	1.8	4.8	5.5	6.6	6.5	..	..	3.2	3.0	4.5	3.4	0.2	5.5	5.0	3.0
	C	1.8	4.3	3.0	5.5	6.2	..	..	3.6	2.8	4.7	2.5	0.2	6.2	5.7	3.1
Salt method	A	1.0	2.6	4.7	5.5	5.1	3.7	3.7	3.3	2.7	4.2	3.9	0.2^a	6.1	5.4	2.9

^{a} Base number.

analysts was held and the points of the procedure were thoroughly discussed. A number of samples were then retested and the results are shown in Table II.

It was apparent, based on the results reported in Tables I and II, that, even after conference periods, this two-phase titration could not be written so that analysts in the same laboratory could obtain reproducible results. That different laboratories would be any more successful was too much to expect.

Table III demonstrated the sensitivity of a two-phase extraction method to experimental technique. On one particular sample, A.S.T.M. D 663-46T was modified as indicated in the table.

These figures showed conclusively that the amount of swirling or mixing during the heating period had a direct influence; the amount of swirling during titration had a greater effect; extraction of the acidic constituents with the prolonged shaking in a closed vessel gave much higher values; and more reproducible results were obtained by titrating the aqueous phase in the absence of oil, but were low.

OTHER METHODS

Because it did not appear possible to standardize the D 663-46T procedure so that reproducible results could be obtained, other possible methods were investigated. Four objectives were sought:

1. The method must be reproducible on both light and dark oils, many of which emulsify easily in contact with aqueous solutions.
2. The method should be simple enough to be carried out with a minimum of training and equipment.
3. The method should be reasonably fast.
4. The results obtained should approach the results obtained by electrometric titration (A.S.T.M. D 664-46T).

The methods studied include three single-phase methods and five two-phase methods, which are described below. Details of the A.S.T.M. methods have been published (*2*, *3*).

A.S.T.M. D 664-46T (Electrometric Method). Titrate the sample, dissolved in a titration solvent made up of benzene and isopropyl alcohol containing 0.5% of water, at room temperature with an alcoholic base or alcoholic-acid solution, using as an indicator the potential between a glass electrode and a calomel reference electrode. Conduct the titration slowly under equilibrium conditions in order to allow complete reaction with all the acidic or basic constituents present.

α-Naphtholbenzein Color Indicator Method. Titrate the sample, dissolved in the same titration solvent as D 664-46T, at room temperature with alcoholic base or alcohol-acid solution using α-naphtholbenzein as an indicator. This has become A.S.T.M. D 974-48T.

Table V. Comparison of Acid Numbers by Different Chemists

	α-Naphtholbenzein Method, Average		Alkali Blue Method, Average	
Sample	Unacquainted	Acquainted	Unacquainted	Acquainted
S-175	2.13	2.11	2.33	2.17
S-176	0.33	0.29	0.24	0.33
S-177	2.92	2.83	3.04	2.73
S-178	3.52	3.35	3.04	3.21
13-1	19.91	19.2	20.1	18.8
13-2	1.60	1.41	2.79	1.39

Alkali Blue Method (Institute of Petroleum IP 1/44 Method A). Weigh a 10-gram sample into a 250-ml. Erlenmeyer flask, add 100 ml. of a mixture of 60 ml. of benzene and 40 ml. of 95% ethyl alcohol neutralized to the alkali blue end point to the oil, and dissolve by swirling. Titrate as quickly as possible with aqueous 0.1 *N* potassium hydroxide at a temperature not exceeding 25° C.

A.S.T.M. D 663-46T (Color Indicator Method). Heat the sample in contact with an alcohol-water solution (essentially 50% ethanol) and titrate the resulting two-phase mixture hot with aqueous potassium hydroxide or sulfuric acid, using phenolphthalein as an indicator. Carry out the titration within 60 to 90 seconds and at a specified degree of agitation.

A.S.T.M. D 663-46T (Butyl Cellosolve Substituted for Alcohol). This is the same as D 663-46T, except for the substitution of butyl Cellosolve for the alcohol in the extracting solution.

Naphtha-Alcohol Method (Standard Oil Company of New Jersey). Weigh into a 300-ml. Erlenmeyer flask 10 to 30 grams of new oil or 1 to 10 grams of used oil, and add 50 ml. of naphtha and 50 ml. of ethyl alcohol neutralized to a phenolphthalein end point. Titrate with 0.1 *N* alcoholic potassium hydroxide added from a 10-ml. buret, graduated in 0.05 ml., to a sharp pink end point with violent agitation of the stoppered flask. Observe the color change in the alcoholic layer. Add the titrant 0.01 ml. at a time where results are low and when near the end point with agitation after each addition.

Table VI. Data

(A.S.T.M. acid and base

	Laboratory A				Laboratory B				Laboratory C				Laboratory D			
Sample	A.S.T.M. D 664	A.S.T.M. D 663	α-Naph-thol-benzein	Alkali blue	A.S.T.M. D 664	A.S.T.M. D 663	α-Naph-thol-benzein	Alkali blue	A.S.T.M. D 664	A.S.T.M. D 663	α-Naph-thol benzein	Alkali blue	A.S.T.M. D 664	A.S.T.M. D 663	α-Naph-thol-benzein	Alkali blue
4-47	Nil	Nil	Nil	Nil	0.01	0.01	0.02	<0.01	Nil	Nil	Nil	Nil	0.00	0.03	0.01	0.02
	Nil	Nil	Nil	Nil	0.01	0.01	0.02	<0.01	Nil	Nil	Nil	Nil	0.00	0.03	0.01	0.02
	Nil	Nil	Nil	Nil	0.01	0.01	0.02	<0.01	Nil	Nil	Nil	Nil	0.00	0.05	0.00	0.02
Av.	Nil	Nil	Nil	Nil	0.01	0.01	0.02	<0.01	Nil	Nil	Nil	Nil	0.00	0.04	0.01	0.02
5-47	Nil	Nil	Nil	Nil	0.01	0.00	0.00	0.02	Nil	Nil	Nil	Nil	0.00	0.00	0.01	0.02
	Nil	Nil	Nil	Nil	0.01	0.00	0.00	0.02	Nil	Nil	Nil	Nil	0.00	0.00	0.01	0.02
	Nil	Nil	Nil	Nil	0.01	0.00	0.00	0.02	Nil	Nil	Nil	Nil	0.00	0.00	0.01	0.01
					0.01											
Av.	Nil	Nil	Nil	Nil	0.01	0.00	0.00	0.02	Nil	Nil	Nil	Nil	0.00	0.00	0.01	0.02
6-47	Nil	Nil	0.01	0.01	0.01	0.04	0.04	0.02	Nil	0.07	0.01	0.00	0.00	0.04	0.02	0.01
	Nil	Nil	0.02	0.01	0.01	0.04	0.04	0.02	Nil	0.04	0.01	0.01	0.00	0.04	0.02	0.01
	Nil	Nil	0.01	0.01	0.01	0.04	0.04	0.02	Nil	0.04	0.01	0.01	0.00	0.05	0.01	0.01
					0.01											
Av.	Nil	Nil	0.01	0.01	0.01	0.04	0.04	0.02	Nil	0.05	0.01	0.01	0.00	0.04	0.02	0.01
7-47	1.26	0.38	1.29	1.24	1.28	1.20	1.24	1.31	1.28	1.24	1.30	1.19	1.32	1.22	1.32	1.27
	1.30	0.39	1.20	1.19	1.28	1.20	1.22	1.32	1.28	1.19	1.29	1.04	1.33	1.24	1.36	1.29
	1.27	0.45	1.28	1.21	1.29	1.20	1.23	1.32	1.32	1.16	1.29	1.19	1.23	1.27	1.35	1.31
						0.95										
						1.07										
Av.	1.28	0.41	1.26	1.21	1.28	1.12	1.23	1.32	1.29	1.20	1.29	1.14	1.29	1.24	1.34	1.29
8-47	2.76	1.69	2.27	2.32	3.35	..	..	..	3.72	2.44	3.13	2.43	3.63	1.97	3.22	2.45
	3.07	1.59	2.20	2.15	3.36	..	..	..	3.85	2.52	3.31	2.42	3.77	1.91	3.24	2.35
	3.11	1.52	2.21	2.31	3.14	..	..	..	3.55	2.40	3.21	2.44	3.71	2.00	3.27	2.35
	3.40				3.15	..	..	..	3.72						3.16	
					3.43	..	..	..								
Av.	3.09	1.60	2.23	2.26	3.27	..	..	..	3.71	2.45	3.22	2.43	3.70	1.96	3.22	2.38
9-47	2.16	1.77	1.87	2.15	2.35	..	..	..	2.29	2.16	2.29	2.28	2.27	1.95	2.14	2.11
	2.14	1.71	1.85	2.20	2.25	..	..	..	2.44	2.30	2.29	2.34	2.30	1.96	2.11	2.15
	2.17	1.69	1.85	2.21	2.35	..	..	..	2.44	2.19	2.28	2.28	2.24	1.92	2.17	2.09
					2.41	..	..	..							2.18	
Av.	2.16	1.72	1.86	2.19	2.34	..	..	..	2.39	2.22	2.29	2.30	2.27	1.94	2.15	2.12
10-47	2.14	0.55	2.01	2.17	2.60	1.13	2.80	2.08	2.33	1.37	2.30	1.79	2.61	0.93	2.17	1.99
	2.06	0.63	2.08	1.99	2.61	1.07	3.07	2.10	2.34	1.34	2.35	1.98	2.58	0.84	2.32	1.94
	2.12	0.79	2.03	1.92	2.79	1.10	3.13	2.17	2.41	1.46	2.24	1.86	2.46	0.86	2.08	1.85
					2.74			2.14						0.89		1.79
																1.81
Av.	2.11	0.66	2.04	2.03	2.68	1.10	3.00	2.12	2.36	1.38	2.30	1.88	2.55	0.88	2.26	1.88
11-47	1.17	0.34	1.39	1.07	..	..	..	..	1.60	0.85	1.57	1.38	1.41	0.49	1.45	1.34
	1.13	0.37	1.38	1.17	..	..	..	..	1.67	0.81	1.65	1.29	1.43	0.44	1.39	1.35
	1.16	0.35	1.44	1.05	..	..	..	..	1.62	0.84	1.56	1.23	1.44	0.38	1.45	1.27
														0.41		
Av.	1.15	0.35	1.40	1.10	..	..	..	..	1.63	0.83	1.59	1.30	1.43	0.43	1.43	1.32
12-47	1.44	0.56	0.85	0.90	..	..	..	..	1.55	0.74	1.25	1.07	1.54	0.51	1.36	1.06
	1.45	0.48	0.86	0.91	..	..	..	..	1.65	0.73	1.27	1.07	1.58	0.54	1.38	1.19
	1.50	0.56	0.96	0.88	..	..	..	..	1.67	0.74	1.26	1.06	1.53	0.48	1.36	1.32
														0.47	1.37	
Av.	1.46	0.53	0.88	0.90	..	..	..	..	1.62	0.74	1.26	1.07	1.55	0.50	1.37	1.19
13-47	2.02	1.35	2.24	1.81	2.81	2.07	3.04	2.32	3.11	1.58	2.74	2.01	3.35	1.49	2.71	2.06
	2.09	1.78	2.40	1.76	2.83	1.95	3.01	2.39	3.28	1.68	3.03	2.10	3.97	1.53	2.60	1.62
	2.11	1.06	2.41	2.02	3.36	1.97	3.10	2.21	3.24	1.68	2.60	2.04	3.59	1.63	2.70	1.90
	2.14			2.04	3.18				3.25				3.15			2.17
	2.21				3.20											
					3.20											
Av.	2.11	1.40	2.35	1.91	3.10	2.00	3.05	2.31	3.22	1.65	2.79	2.05	3.52	1.55	2.67	1.94
14-47	2.18	1.39	1.87	1.89	3.28	1.95	2.58	2.15	3.13	1.45	2.92	2.04	3.44	1.80	2.45	1.94
	2.21	1.76	1.91	1.94	3.11	1.82	2.49	2.03	3.12	1.71	2.69	2.14	3.33	1.80	2.73	1.83
	2.19	1.49	1.92	2.10	2.93	1.83	2.46	1.96	3.18	1.61	2.62	2.11	3.00	1.41	2.56	2.08
	1.96				2.97				3.16				2.74	1.61		1.95
					2.87											
					2.86											
Av.	2.13	1.55	1.90	1.98	3.00	1.87	2.51	2.05	3.15	1.59	2.74	2.10	3.13	1.66	2.58	1.95

Whiting Method [Standard Oil Company (Indiana)]. Add 200 ml. of cleaner's naphtha and 100 ml. of 95% ethyl alcohol to a 500-ml. glass-stoppered Erlenmeyer flask. Neutralize by adding 1 ml. of phenolphthalein solution and titrate to the first pink in the alcoholic layer with agitation during neutralization. Weigh into the flask 50 grams of a new or clear oil, or 5 grams of a dark oil. Titrate to the first color change toward pink of the alcoholic layer with violent agitation of the stoppered flask between additions of sodium hydroxide. Allow liquids to break before observing color. In difficult cases, warm the flask to break the emulsion.

Salt Procedure [Standard Oil Company (Indiana)]. Weigh 5 grams of oil into a 250-ml. glass-stoppered Erlenmeyer flask, add 20 ml. of neutralized naphtha, and agitate to bring the oil into solution. Add 40 ml. of neutralized saturated aqueous solution of sodium chloride and 40 ml. of neutralized 95% ethyl alcohol. Heat to boiling in unstoppered flask and boil 1 minute. Add phenolphthalein solution and titrate with aqueous 0.1 *N* potassium hydroxide with vigorous shaking until the pink color of the end point persists for 30 seconds after 5 seconds of vigorous shaking.

In Table IV, the results of this cooperative work are tabulated. It was evident from this work that the single-phase α-naphtholbenzein and alkali blue methods met most of the requirements originally set. They were reproducible, simple, and rapid, and gave results comparable to the electrometric method. Brief comments on these points received from members of the cooperating laboratories are summarized below.

Previous work with D 663–46T (see Table I) had shown the lack of reproducibility. Correspondence addressed to the author, as chairman of the A.S.T.M. subcommittee, had shown that the method could not be carried out in the time specified, and that the end point was difficult to see. There was also no relation between the results obtained and electrometric results.

The modification using butyl Cellosolve did not improve the situation. Furthermore, it was found that butyl Cellosolve separated to form a third phase upon heating.

The naphtha-alcohol method failed to meet the criteria of speed and comparable results. Therefore, further work to check the reproducibility was not carried out. It was found that 54° A.P.I. naphtha gave somewhat better separation of emulsions than 72° A.P.I.

Summary

number cooperative survey)

Laboratory E				Laboratory F				Laboratory G			
A.S.T.M. D 664	A.S.T.M. D 663	α-Naphtholbenzein	Alkali blue	A.S.T.M. D 664	A.S.T.M. D 663	α-Naphtholbenzein	Alkali blue	A.S.T.M. D 664	A.S.T.M. D 663	α-Naphtholbenzein	Alkali blue
Nil	Nil	Nil	Nil	Nil	0.03	0.01	0.01	0.02	0.02	0.01	0.01
Nil	Nil	Nil	Nil	Nil	0.02	0.01	0.01	0.03	0.02	0.01	0.01
Nil	Nil	Nil	Nil	Nil	0.02	0.01	0.01	0.02	0.02	0.01	0.01
Nil	Nil	Nil	Nil	Nil	0.02	0.01	0.01	0.02	0.02	0.01	0.01
Nil	Nil	Nil	Nil	Nil	0.01	0.01	0.01	0.02	0.01	0.01	0.01
Nil	Nil	Nil	Nil	Nil	0.02	0.01	0.01	0.02	0.01	0.01	0.01
Nil	Nil	Nil	Nil	Nil	0.01	0.01	0.01	0.02	0.01	0.01	0.01
Nil	Nil	Nil	Nil	Nil	0.01	0.01	0.01	0.02	0.01	0.01	0.01
Nil	0.03	0.02	0.01	Nil	0.03	0.02	0.02	0.02	0.02	0.02	0.01
Nil	0.02	0.02	0.02	Nil	0.04	0.02	0.03	0.03	0.02	0.02	0.01
Nil	0.03	0.02	0.02	Nil	0.03	0.02	0.02	0.02	0.02	0.02	0.01
Nil	0.03	0.02	0.02	Nil	0.03	0.02	0.02	0.02	0.02	0.02	0.01
1.34	1.21	1.28	1.08	1.37	1.14	1.26	1.37	1.28	1.05	1.32	1.04
1.35	1.24	1.29	1.09	1.39	1.19	1.24	1.17	1.28	1.15	1.35	1.05
1.33	1.25	1.30	1.10	1.35	1.12	1.25	1.30	1.30	1.25	1.37	1.09
1.34	1.23	1.29	1.09	1.37	1.15	1.25	1.28	1.29	1.15	1.35	1.06
3.42	1.68	2.91	2.62	4.41	1.62	3.12	2.39	3.51	1.20	2.87	1.95
3.12	1.72	2.92	2.57	4.10	1.51	3.58	2.34	3.55	1.25	2.90	2.00
3.25	1.70	2.88	2.51	4.26	1.68	3.06	2.44	3.58	1.35	3.00	2.05
3.26	1.70	2.90	2.57	4.26	1.60	3.25	2.39	3.55	1.27	2.92	2.00
2.24	1.91	2.24	2.24	2.02	1.85	2.06	2.18	2.17	1.75	2.10	1.93
2.28	2.03	2.24	2.19	2.18	1.89	2.11	2.48	2.18	1.85	2.11	1.98
2.27	1.90	2.17	2.22	2.18	1.95	2.01	2.22	2.21	1.90	2.11	1.98
2.26	1.95	2.22	2.22	2.13	1.90	2.06	2.29	2.19	1.82	2.11	1.96
2.22	1.07	2.36	2.11	3.04	0.93	2.07	1.90	2.31	0.80	1.93	1.55
2.25	1.08	2.24	2.01	2.82	0.90	1.89	2.17	2.31	0.85	2.12	1.58
2.33	1.17	2.29	1.96	2.99	0.82	2.11	2.17	2.32	0.90	2.23	1.62
2.27	1.11	2.30	2.03	2.95	0.88	2.02	2.08	2.31	0.85	2.09	1.58
1.58	0.38	1.84	2.08	1.37	0.54	1.73	1.05	1.42	0.50	1.49	1.38
1.42	0.41	1.91	2.19	1.43	0.50	1.75	1.04	1.45	0.44	1.36	1.47
1.54	0.40	1.93	2.26	1.43	0.45	1.79	1.04	1.48	0.49	1.44	1.43
1.51											
1.51	0.40	1.89	2.18	1.41	0.50	1.76	1.04	1.45	0.48	1.43	1.43
1.41	0.42	1.03	0.64	1.41	0.48	1.02	0.88	1.50	0.55	0.86	0.85
1.51	0.40	1.02	0.65	1.41	0.43	1.04	0.85	1.60	0.45	0.92	0.94
1.46	0.42	0.99	0.65	1.47	0.43	1.02	0.80	1.65	0.50	0.97	0.84
		1.01									
1.46	0.41	1.01	0.64	1.43	0.45	1.03	0.84	1.58	0.50	0.92	0.88
2.79	1.37	2.17	1.80	3.57	1.12	2.81	1.79	3.25	1.80	2.69	2.00
2.87	1.45	2.27	1.95	3.36	1.22	2.53	2.04	3.14	1.70	2.58	2.00
2.83	1.37	2.30	1.92		1.17	2.53	2.29	3.10	1.70	2.58	2.07
2.83	1.40	2.25	1.89	3.47	1.17	2.62	2.04	3.15	1.73	2.62	2.02
2.86	1.42	2.17	1.78	3.36	1.13	2.53	2.04	2.90	1.78	2.33	1.87
2.86	1.34	2.21	1.88	3.30	1.17	2.81	2.29	2.93	1.78	2.48	1.84
2.95	1.46	2.17	1.86		1.07	3.06	2.29	2.95	1.63	2.44	1.96
2.89	1.41	2.18	1.84	3.33	1.12	2.80	2.21	2.93	1.73	2.42	1.89

The Whiting method failed to meet the objectives for the same reasons as the naphtha-alcohol. Dropwise titration when approaching the end point was very time-consuming, because of the slowness with which the layers separate. Warming helps to break the emulsion, but may also cause saponification, as evidenced by the rapid fading of the indicator color upon warming. In some cases, a dense sludge remains in the alcohol layer.

The salt method was an improvement over D 663-46T. The color of the oil did not blend into the aqueous layer, and the end point did not fade so quickly. Emulsification was still a problem on some oils. Although the comparisons with the electrometric results were in general good, inspection of Table IV shows that the single-phase methods gave more consistent correlation.

The two single-phase methods, α-naphtholbenzein and IP 1/44 (alkali blue), appeared promising. The single-phase operation improved the simplicity and speed, and the results were more reproducible, and near enough to the electrometric to encourage further investigation. Further cooperative work was, therefore, carried out on these two methods.

In the course of the work on the single-phase methods, a number of observations were made.

Both alkali blue and α-naphtholbenzein varied in composition. Some of these dyestuffs were not suitable as indicators. Some of the commercial α-naphtholbenzein contained an excess of chlorine which made it unsuitable in nonaqueous titrations.

Alkali blue had to be sensitized by treating with dilute hydrochloric acid and then neutralizing with potassium hydroxide.

The determination of the alkali blue end point was not improved by back-titration. Results by back-titration did not agree with those obtained by direct titration.

Both alkali blue and α-naphtholbenzein gave slightly high results when used by inexperienced analysts. This was attributed to the extreme caution used in approaching end points and in recognizing their persistence. This resulted in a large increase in titration time and shaking, which allowed more than the average amount of carbon dioxide to be dissolved, or permitted excessive saponification to occur. This was particularly true of oils containing a large amount of color and suspended solids, which, when titrated for 15 minutes instead of 1 or 2 minutes, gave end points as much as 1.5 mg. of potassium hydroxide per gram, higher than the first gradually fading end point. The α-naphtholbenzein method was favored by the analysts over the alkali blue because the end points were easier to detect.

In Table V, a comparison between results of analysts who were acquainted with the methods, and those who were unacquainted, is shown to demonstrate this point.

The results of the final survey (Tables VI and VII) make it apparent that two color indicator methods met the objectives outlined above. On the basis of repeatability, reproducibility, speed, and simplicity, either α-naphtholbenzein or alkali blue could have been adopted for A.S.T.M. standardization. Two factors resulted in the adoption of α-naphtholbenzein: the results more consistently approached the electrometric method than did alkali blue, and the operators felt that the α-naphtholbenzein end point was easier to see.

The good repeatability and reproducibility of the old A.S.T.M. D 663-46T method are probably due to the fact that the group carrying out these tests had become expert through close association with the problem. A comparison of Table VI and Table I indicates how long study and manipulation on the part of the cooperating laboratories improved the results by the two-phase method. It is too much to expect that other laboratories would devote similar time and effort to become expert. Results obtained by D 663-46T seldom were comparable to those obtained by the electrometric method.

In acid number titrations of used petroleum oils, the question of

Table VII. Average Results, Repeatability, and Reproducibility

(A.S.T.M. acid and base number cooperative survey)

	A.S.T.M. D 664			A.S.T.M. D 663			α-Naphtholbenzein			Alkali Blue		
Sample	Average result	Repeat-ability	Repro-ducibility	Average result	Repeat-ability	Repro-ducibility	Average result	Repeat-ability	Repro-ducibility	Average result	Repeat-ability	Repro-ducibility
4-47	0.003	0.00	0.005	0.01	0.003	0.01	0.007	0.001	0.006	0.007	0.00	0.006
5-47	0.004	0.00	0.006	0.003	0.001	0.004	0.004	0.00	0.005	0.009	0.001	0.006
6-47	0.007	0.00	0.006	0.003	0.007	0.01	0.02	0.003	0.006	0.01	0.004	0.004
7-47	1.31	0.02	0.03	1.07	0.05	0.19	1.29	0.02	0.03	1.29	0.03	0.10
8-47	3.55	0.16	0.29	1.76	0.07	0.29	2.99	0.10	0.27	2.34	0.06	0.14
9-47	2.25	0.06	0.08	1.93	0.06	0.11	2.12	0.03	0.11	2.18	0.06	0.09
10-47	2.46	0.07	0.23	0.98	0.07	0.19	2.29	0.12	0.21	1.94	0.10	0.14
11-47	1.43	0.03	0.01	0.50	0.02	0.14	1.58	0.03	0.16	1.40	0.04	0.28
12-47	1.52	0.04	0.07	0.52	0.03	0.08	1.08	0.02	0.16	0.93	0.03	0.14
13-47	3.06	0.12	0.33	1.56	0.06	0.20	2.62	0.09	0.18	2.02	0.08	0.09
14-47	2.94	0.08	0.24	1.56	0.09	0.17	2.45	0.11	0.24	2.00	0.08	0.10
	Acid No. Magnitude											
Survey max. 4-47 to 6-47	0.0-0.75	0.0	0.006		0.007	0.01		0.003	0.006		0.0	0.004
A.S.T.M. spec.		0.02	0.03		0.05	0.05		0.05	0.10		0.05	0.10
Survey max. 7-47 to 14-47	0.75-3.0	0.16	0.33		0.09	0.29		0.12	0.27		0.10	0.14
A.S.T.M. spec.		0.10	0.20		0.15	0.37 (35% of mean)		0.10	0.20		0.10	0.20

Table VIII. Saponification Tendency of Test Methods

	A.S.T.M. D 664-46T	A.S.T.M. D 663-46T	α-Naphtholbenzein	Alkali Blue
Actual 14-47	2.94	1.56	2.45	2.00
Calculated 14-47	2.80	1.45	2.41	1.87
Difference	0.14	0.11	0.04	0.13

the amount of saponification taking place is invariably raised. In Tables VI and VII, samples 13-47 and 14-47 were prepared to determine this point. Sample 14-47 is the same oil as sample 13-47, to which was added 10% of prime lard oil having an acid number of 0.5. Because these weak acids blend arithmetically, Table VIII has been prepared to show the actual results obtained on 14-47 and those calculated from the blend of 13-47 and the lard oil.

It is possible that saponification did not cause all the increase in view of the repeatability and reproducibility of the tests. However, the fact that the deviations were constant in one direction indicated that a small amount of saponification did take place. The results obtained by the α-naphtholbenzein method were in surprisingly good agreement.

SUMMARY AND CONCLUSION

Thousands of cooperative tests during the past several years have indicated that no satisfactory method of determining the acidic or basic components present in petroleum lubricating oils by two-phase titration is available. Two single-phase titration methods were found which showed considerable promise, and their development has resulted in simple and fast methods of improved precision. The method using α-naphtholbenzein was adopted because it more consistently gave results similar to those obtained with the electrometric titration.

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Determination of Total Phosphorus in Organic Phosphates

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THE extensive use of organic phosphates as insecticides and for other purposes necessitates a satisfactory method for their chemical analysis. As a basis for rating the insecticidal value of an organic phosphate mixture, a selective method such as the one proposed by Dvornikoff and Morrill (*4*) or the method proposed by Wreath and Zickefoose (*10*) for the determination of tetraethyl pyrophosphate, which is the active insecticidal agent in certain organic phosphate products, is of prime importance, but this excludes other forms of phosphorus which may contribute to the value of the product as, for example, by increasing the total phosphorus uptake by plants (*8*). Jacobson and Hall (*7*) adapted an alkali fusion method to the conversion of organic phosphorus in aliphatic phosphates, then determined the phosphorus colorimetrically by the molybdivanadophosphoric acid method. They found that the method is rapid and accurate and that it involves negligible damage to platinum ware, but they reported no data for aromatic phosphates.

Hardin and MacIntire (*6*) demonstrated that whereas the official A.O.A.C. procedures register the full phosphorus content of all tested fertilizers, those procedures register only fractional values for certain concentrated organic phosphates. They succeeded in transforming the phosphorus in hexaethyl tetraphosphate to ionized orthophosphate by digesting an aliquot that contained 0.04 gram in 10 ml. of water with 5 ml. of hydrochloric acid and 5 ml. of nitric acid for a period of 16 hours at 120° C. Prolongation of the digestion period to 24 hours effected complete

Two independent procedures for the conversion of organic phosphorus into ionized orthophosphate are adapted to the volumetric determination of phosphorus by the molybdiphosphate-alkalimetric method. One procedure is based upon the reaction with hydriodic acid; the other is based upon destructive oxidation with a mixture of nitric, perchloric, and sulfuric acids in the presence of a molybdenum catalyst.

conversion of triethyl phosphate and monoethyl phosphate, but only partial conversion of two samples purported to be tritolyl phosphate and triphenyl phosphate. Wreath (*9*) has reported the use of perchloric-nitric acid mixtures on some samples of organic phosphates after first checking the results against those obtained by Parr bomb combustion. In the present paper two distinctive methods are presented for the conversion of organic phosphates, both aliphatic and aromatic, and in each case the analysis is completed by the A.O.A.C. molybdiphosphate-alkalimetric titration procedure (*1*).

The first method is based upon reaction with concentrated hydriodic acid. No attempt to use this reagent in the analysis of organic phosphates has been reported. Its possibility was indicated by the results obtained by Fleury, Courtois, and Desjobert (*5*) in their study of the rates of hydrolysis of ethyl and glycol phosphates. They found that for a given normality (1 to 10 *N*) the rate of hydrolysis increased with the presence of the acid in the order sulfuric, hydrochloric, hydrobromic, and hydriodic.

The second method is based upon oxidation with a mixture of perchloric, sulfuric, and nitric acids in the presence of sodium molybdate as a catalyst. Although this method for the decomposition of organic phosphates has not been reported, it has been proposed by Bolin and Stambery (*3*), but without the addition of nitric acid, for the analysis of various agricultural feed materials.

SPECIAL REAGENTS

Hydriodic acid, C.P. grade, specific gravity 1.7, 55, 58%.

Sodium molybdate–sulfuric acid–perchloric acid oxidation mixture. Dissolve 35 grams of sodium molybdate dihydrate in 150 ml. of water. Add 150 ml. of concentrated sulfuric acid and 200 ml. of concentrated perchloric acid.

PROCEDURE

Hydriodic Acid Conversion. Weigh 0.25 to 0.30 gram of organic phosphate into a 500-ml. Kjeldahl flask containing 30 ml. of concentrated hydriodic acid and several boiling stones. Attach a water condenser and reflux for the period indicated as adequate, in Table IV. Wash the condenser tube with distilled water and dilute to 100 ml. To avoid interference in the subsequent determination of phosphorus, destroy the hydriodic acid by cautiously adding 30 ml. of concentrated nitric acid and swirling the flask; then warm very gently to prevent boiling over from the rapid escape of oxides of nitrogen entrained in the precipitated iodine, and boil to a volume of 100 ml. to remove the last traces of iodine. Transfer to a 250-ml. volumetric flask and dilute to the mark. The aliphatics give colorless solutions but the aromatics give solutions which vary in color from pale green to pale orange. Determine the phosphorus in aliquots by the molybdiphosphate-alkalimetric method using the A.O.A.C. procedure (*1*). For percentages between 30 and 60, a 25-ml. aliquot is recommended and below 30% a 50-ml. aliquot. Add a small piece of litmus paper, make slightly alkaline with ammonia, cool, and make just acid with nitric acid.

Catalytic Oxidation. Weigh 0.25 to 0.30 gram of organic phosphate into a 500-ml. Kjeldahl flask containing 5 ml. of catalytic oxidation mixture (*3*). Add 10 ml. of concentrated nitric acid, 10 to 20 glass beads, and several boiling stones. Boil 15 minutes, then add 2 ml. of perchloric acid and continue to boil until dense white fumes have been evolved for a minute, which should require an additional 15 minutes. Transfer to a 250-ml. volumetric flask and dilute to the mark. The glass beads may be removed easily by pouring the liquid and beads onto a perforated porcelain disk or a Gooch type of crucible placed in a small funnel and draining into the volumetric flask. Determine

Table I. Hydriodic Acid Conversion of Phosphorus in Aliphatic Phosphates

Reflux Period with Hydriodic Acid, Hours	Hexaethyl tetra	Hexaethyl tetra	Monoethyl	Monoethyl	Tetraethyl pyro base[a]	Tributoxy ethyl	Triethyl	Triethyl	Vapotone[b]
	P_2O_5 Content by Molybdiphosphate-Alkalimetric Method, %								
0.08	55.6	54.5	54.9	56.2	48.5	16.9[c]	37.6	38.3	..
0.25	55.7	54.9	55.1	56.3	48.3	17.5	37.7	37.8	..
0.5	..	..	..	..	..	17.6	37.6	37.2	..
0.75	..	..	..	..	..	17.7	38.1	..	..
1	55.6	..	..	..	48.7	17.5	37.9	..	13.7[c,d]
2	55.8	..	..	..	48.8	17.6	37.8	..	15.8[c,d]
2	55.8	..	..	..	48.9	17.3	37.2	..	..
2	55.7	..	..	..	48.5	17.3	37.2	..	..
3	..	..	..	..	..	..	..	..	15.4[c,d]
4	..	..	..	..	..	..	..	..	24.5[c]
5	..	..	..	..	..	..	..	..	40.0[c]
6	..	..	..	..	..	..	..	..	43.3
7	..	..	..	..	..	..	..	..	43.0
8	..	..	..	..	..	..	..	..	43.6
Mean	55.7	54.7	55.0	56.2	48.6	17.5	37.6	37.8	43.3

[a] Technical tetraethyl pyrophosphate.
[b] 50% technical tetraethyl pyrophosphate with an organic solvent and emulsifier.
[c] Recovery considered incomplete, not averaged.
[d] Results verified by molybdivanadophosphoric acid method. Irregular progression of recovery attributed to immiscibility of sample with reagent and variations in surface area corresponding to differences in sample weights

Table II. Hydriodic Acid Conversion of Phosphorus in Aromatic Phosphates

Reflux Period with Hydriodic Acid, Days	Triphenyl[a]	Triphenyl	Tri-*o*-cresyl	Tri-*m*-cresyl	Tri-*p*-cresyl	Tricresyl[b]	Tri-*o*-phenyl phenyl
	P_2O_5 Content by Molybdiphosphate-Alkalimetric Method, %						
4 hours	9.8	7.9	..	..	..	..	..
8 hours	18.6	20.5	..	..	..	..	..
12 hours	21.4	21.1	..	..	..	..	..
16 hours	21.2	21.2	..	..	..	..	..
1	..	..	8.1	8.7	8.1	3.1	0.9
2	..	..	13.9	14.9	11.8	10.2	3.0
3	..	..	18.3	18.1	14.8	11.3	..
4	..	..	18.9	17.9	17.5	13.3	3.5
5	..	..	20.0	19.3	18.9	13.9	5.8
6	..	..	19.4	18.7	19.0	14.7	6.1
7	..	..	19.4	19.1	19.4	17.4	..
8	..	..	19.8	18.2	18.7	17.2	9.3
9	..	..	..	..	..	..	10.5
10	..	..	..	..	..	..	10.6
11	..	..	..	..	..	..	11.3
12	..	..	..	..	..	..	12.3
13	..	..	..	..	..	..	11.4
14	..	..	..	..	..	..	11.1
15	..	..	..	..	..	..	11.6
16	..	..	..	..	..	..	12.6
Mean[c]	21.3	21.1	19.5	18.6	19.0	17.3	11.7

[a] Recrystallized twice from methanol and water.
[b] Isomer not specified, but identified through derivatives as chiefly meta isomer.
[c] Mean of values below lines after apparent conversion.

Table III. Effect of Additional Oxidation on Hydriodic Acid Conversion of Organic Phosphates

(P_2O_6 content found after 3 minutes' digestion with oxidizing agent)

	Perchloric Acid, %	Ammonium Persulfate, %	None, %
Hexaethyl tetra	55.7	56.3	56.4
Hexaethyl tetra	55.3	55.3	55.0
Monoethyl	54.6	54.7	54.5
Monoethyl	56.1	56.1	56.0
Tetraethyl pyrobase[a]	47.9	48.0	47.6
Tributoxy ethyl	17.5	17.5	17.5
Triethyl	37.4	37.2	37.4
Triethyl	38.0	38.0	37.9
Vapotone[b]	44.2	44.1	44.1
Triphenyl[c]	21.5	21.6	21.3
Triphenyl	21.5	21.6	21.5
Tri-*o*-cresyl	16.7	16.8	16.7
Tri-*m*-cresyl	17.7	17.6	17.6
Tri-*p*-cresyl	17.9	17.7	17.7
Tricresyl	17.0	17.0	17.0
Tri-*o*-phenyl phenyl	12.5	12.4	12.4

[a] Technical tetraethyl pyrophos phate.

[b] 50% technical tetraethyl pyrophosphate with organic solvent and emulsifier.

[c] Recrystallized twice from methanol and water.

the phosphorus in aliquots by the molybdiphosphate-alkalimetric method using the A.O.A.C. procedure (*1*).

DISCUSSION

Hydriodic Acid Conversion. The data in Table I show that with the exception of tributoxy ethyl phosphate, refluxing with hydriodic acid for 5 minutes effected complete conversion of phosphorus or so nearly complete that this was achieved in the next step of digestion with nitric acid. Conversions of aromatic phosphates required as long as a week, or even more, as is shown in Table II.

To determine whether the addition of an oxidizing agent other than nitric acid would alter the results of analysis, a sample of each of the sixteen organic phosphates studied was treated with hydriodic acid as described and three identical aliquots were taken. In each series one aliquot was boiled 3 minutes with 0.5 ml. of 72% perchloric acid, the second aliquot was boiled 3 minutes with the addition of 0.3 gram of ammonium persulfate, and the third was given no additional treatment. The phosphorus pentoxide content of each portion was then determined by the A.O.A.C. (*1*) method. The results recorded in Table III show that in each series of aliquots, for both aliphatics and aromatics, the additional digestion with perchloric acid or with ammonium persulfate is unnecessary.

Individual runs with most of the aliphatic phosphates (Table I) gave checks within 0.1 to 0.2% of the mean, whereas with the aromatics (Table II) individual runs varied as much as 0.9% from the mean. The standard deviation was 0.2% for the aliphatics and 0.4% for the aromatics.

Blumenthal and Herbert (*2*) have shown that the acid hydrolysis of methyl phosphate involves the splitting of the *O*-methyl bond. Although this reaction may not be strictly analogous to the reaction between hydriodic acid and aliphatic phosphates, it is presumed that in the latter case the cleavage is similar. As a check upon the nature of the reaction between hydriodic acid and aromatic phosphates, phenol was isolated from the triphenyl phosphate and cresol was isolated from each of the four tricresyl phosphates. In each case identification of the phenolic variety was confirmed through two of its derivatives, tribromophenol and phenoxyacetic acid for phenol itself and the corresponding aryloxyacetic acids and 2,4-dinitrophenyl ethers for the three cresols. Although the isomer present in the sample labeled tricresyl phosphate was not disclosed by the manufacturer, the two derivatives proved it to be composed chiefly of the meta isomer.

Catalytic Oxidation. Conversion of the organic phosphates studied was found to be complete within 30 minutes. The method involves complete destruction of organic matter which is purported to interfere with the determination of phosphorus by the molybdiphosphate-alkalimetric method employed. The means of results of all determinations obtained through use of the catalytic oxidation method of conversion are given in Table IV, in which a comparison of the two methods of conversion is also given.

Duplicate runs agreed within 0.1 to 0.2% of the mean for both the aliphatic and the aromatic phosphates. The standard deviation was 0.3% for the aliphatics and 0.1% with the aromatics. The rapidity and completeness of the destruction of organic matter effected by catalytic oxidation favor this method of conversion and it is recommended for both aliphatic and aromatic phosphates.

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Table IV. Comparison of Hydriodic Acid and Catalytic Oxidation Methods for Determination of Phosphorus in Organic Phosphates

	Theoretical P_2O_5 Equivalent[a], %	Hydriodic Acid Method		Catalytic[b] Oxidation Method, P_2O_5 Found, %
		Reflux period, Min.	P_2O_5 found, %	
Hexaethyl tetra	56.1	5	55.7	55.7
Hexaethyl tetra	56.1	5	54.7	56.8
Monoethyl	56.3	5	55.0	56.4
Monoethyl	56.3	5	56.2	57.2
Tetraethyl pyrobase[c]	48.9	5	48.6	48.4
Tributoxy ethyl	17.8	15	17.5	17.4
Triethyl	38.9	5	37.6	37.9
Triethyl	38.9	5	37.8	37.9
Vapotone[d]		6 hours	43.3	44.8
Triphenyl[e]	21.8	12 hours	21.3	21.8
Triphenyl	21.8	12 hours	21.1	20.7
Tri-*o*-cresyl	19.2	4 days	19.5	18.8
Tri-*m*-cresyl	19.2	3 days	18.6	19.9
Tri-*p*-cresyl	19.2	5 days	19.0	20.0
Tricresyl	19.2	7 days	17.3	18.7
Tri-*o*-phenyl phenyl	12.8	11 days	11.7	13.1

[a] Upon basis of 100% purity.

[b] Maximum duration 30 minutes.

[c] Technical tetraethyl pyrophosphate.

[d] 50% technical tetraethyl pyrophosphate with organic solvent and emulsifier.

[e] Recrystallized twice from methanol and water.

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Determination of Oxygen in Titanium

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Modified vacuum fusion techniques have been employed for the determination of oxygen in titanium. The sample to be analyzed reacts with powdered graphite, in the presence of tin, to form the stable carbide of titanium and reduce the oxides. The evolved gases are extracted and analyzed. With a furnace temperature of 1900° C., complete reduction is effected within 30 minutes. Good blank conditions are achieved. The analysis of synthetic standards, prepared by diffusing oxygen gas into hot titanium metal, indicates practically complete recovery of oxygen. Analyses have been made on titanium samples which have been prepared by commercial processes. The vacuum apparatus is illustrated and described, and details for the preparation of standard reference samples are given.

WITH the development of improved commercial processes for the production of high purity titanium metal, it has become necessary to devise and refine analytical techniques for the determination of all elements whose presence might affect the physical properties of the metal. Foremost in importance among the contaminating constituents are the major atmospheric gases, which can be introduced during the metal's fabrication as well as during its production. It is generally agreed that these gases have marked effects upon the physical properties of titanium, but accurate correlations have awaited the development of dependable analytical methods for the determination of the gas content.

Wet chemical methods for the determination of nitrogen in ferrous metals have been studied extensively (*8*), and adaptations of existing methods can be made for a sufficiently accurate evaluation of the nitrogen content of titanium. Oxygen, however, has been more adept at eluding the analytical chemist.

Among the various methods used for determining oxygen in metals, the vacuum fusion method has been the most satisfactory in general, and this was chosen as the method offering most promise for the work described here. The vacuum apparatus was designed primarily for the oxygen-titanium investigation, but attention was given also to incorporating features that would make it an apparatus of general applicability and a versatile research tool.

The investigation on oxygen in titanium was undertaken by the Metallurgy Division of the Naval Research Laboratory as a vital supplement to its titanium research program. A dependable method for determining oxygen was considered a prerequisite for an accurate survey of the possibilities and limitations of titanium as a structural metal.

The method which has been developed suggests many possibilities for further investigations, but the interest shown in the work already completed has made it seem expedient to release the method in its present form.

EXPERIMENTAL INVESTIGATION

The analytical investigation was begun along the lines of established vacuum fusion practice, in which the metal sample is melted in an induction-heated graphite crucible, thereby reducing the oxides and decomposing the hydrides and nitrides thermally (*1–3*). The gaseous products of the reactions—carbon monoxide, hydrogen, and nitrogen—are extracted from the reaction crucible and analyzed. The gas pickup characteristics of hot titanium, however, made it impossible to extract more than a small fraction of the theoretical amount of carbon monoxide. Some investigators have reported favorable oxygen recoveries by diluting the titanium with large amounts of iron, but it was impossible in this investigation to duplicate their achievements or to establish the exact conditions necessary for complete recovery of the oxygen by numerous variations of their technique. Not more than 50% of the oxygen could be recovered, but this was not a consistent figure. It varied with the sample size, the physical state of the sample, and the type of oxidation to which the sample had been subjected.

It was apparent that a new approach to the problem was needed, and attention was given to the possibility of eliminating completely the gas pickup characteristics of titanium either by removing the mass of the active metal, after converting it to a volatile salt, as is done in the residue method of oxygen in metals (*9*), or by forming a compound of titanium which would be stable at high temperatures and inert with respect to gas pickup. The latter possibility offered the advantages of simplicity and convenience, in that titanium carbide, which has the desired properties of stability and inertness, could be formed in the reaction crucible with only minor modifications of the existing vacuum equipment. Furthermore, the carbide formation would proceed with a simultaneous reduction of the oxides of titanium. Under these conditions, it seemed reasonable to expect a satisfactory evolution of carbon monoxide without troublesome side reactions.

Preliminary work, in which a titanium sample of known oxygen content reacted with powdered graphite in a graphite crucible, indicated that the reaction between titanium and carbon proceeded quantitatively, forming titanium carbide (TiC). The oxygen evolved as carbon monoxide was approximately 75% of the amount added.

In vacuum fusion work with steels containing high percentages of aluminum and manganese, some investigators have reported correspondingly low oxygen recoveries. This difficulty was overcome to a great extent by the addition of metallic tin to the molten bath (*9*). Small additions of tin to the reaction crucible in this work produced an analogous improvement resulting in oxygen recoveries as great as 90% (Table I).

Table I. Analysis of Titanium Standards

(No tin fusion)

Sample No.	Sample Weight	Oxygen Added	Oxygen Recovered
	Gram	%	%
1	0.327	0.65	0.60
2	0.385	0.50	0.45
3	0.364	0.39	0.36
4	0.364	0.18	0.16

On the basis of the findings of Kroll and Schlechton (*6*), it was believed that the remaining 10% of oxygen was retained within the titanium carbide cinder. These investigators, attempting to reduce metal oxides with carbon under high vacuum, reported that the main difficulty encountered was the sintering of the metal, which sealed up the voids through which the carbon monoxide could escape. It was hoped that this condition could be overcome, if it existed, by fusing the titanium sample with tin before the carbide reaction could be initiated, thus distributing the titanium metal over a greater surface of graphite, with a resulting greater porosity of the carbide structure.

This was tried with favorable results. Standard samples, prepared by the addition of pure titanium dioxide to titanium metal, as well as samples prepared by the addition of gaseous oxygen, gave recoveries above 97% (Table II).

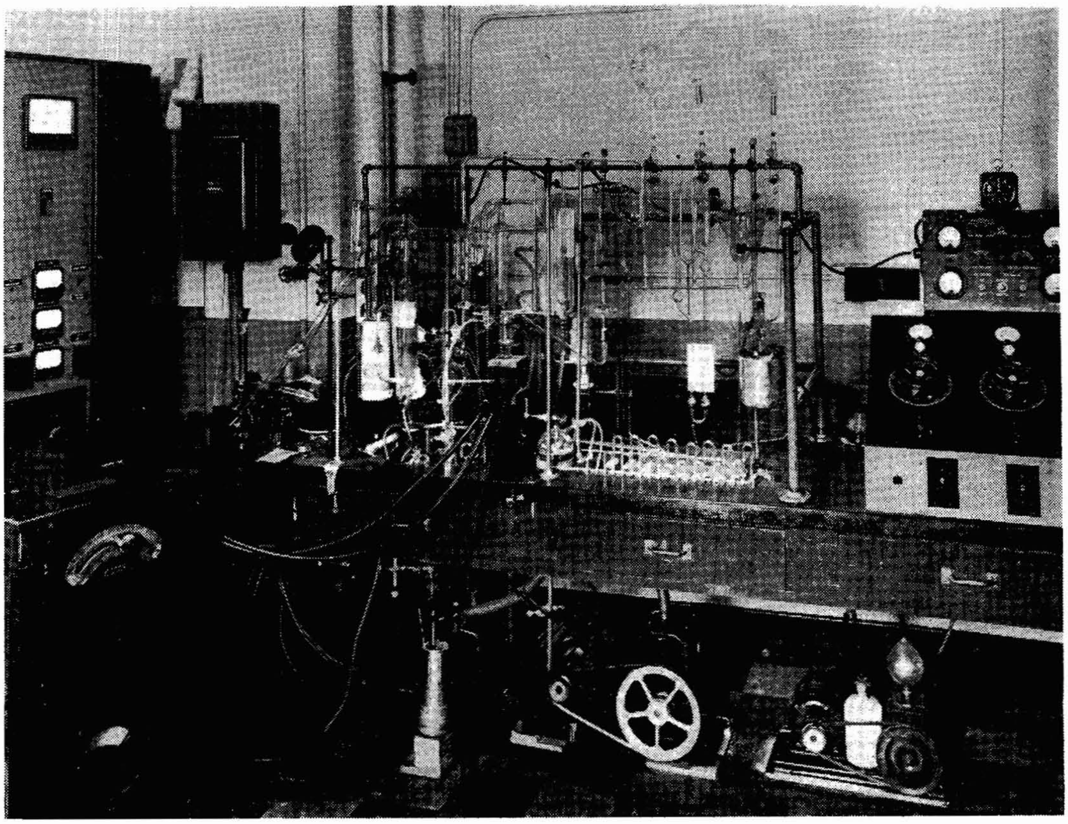

Figure 1. Photograph of Complete Apparatus

APPARATUS

The vacuum apparatus, pictured in Figure 1 and illustrated schematically in Figure 2, is constructed entirely of borosilicate glass. It consists of a furnace unit and an analytical unit, fused together to form one continuous system. With the exception of the furnace exhaust tube, which has an outside diameter of 25 mm., all connecting tubing is 15 mm. This large tubing provides for rapid pumping of the gases and contributes to the rigidness and stability of the apparatus. A suspension type of supporting framework is used to facilitate flaming of the apparatus and to eliminate the development of strains in the glass.

Two oil-sealed mechanical pumps are used: a high-speed pump, connected to T_4, provides the backing for the high vacuum system; and a smaller pump maintains an auxiliary vacuum system, not illustrated, which operates the McLeod gage, G_2, and the mercury cutoffs, C_1 to C_{10}.

Mercury Cutoffs. Mercury cutoffs have been used in place of stopcocks in the high vacuum system, with the exception of stopcock S_1 (Figure 2), which is used to seal off the vacuum system

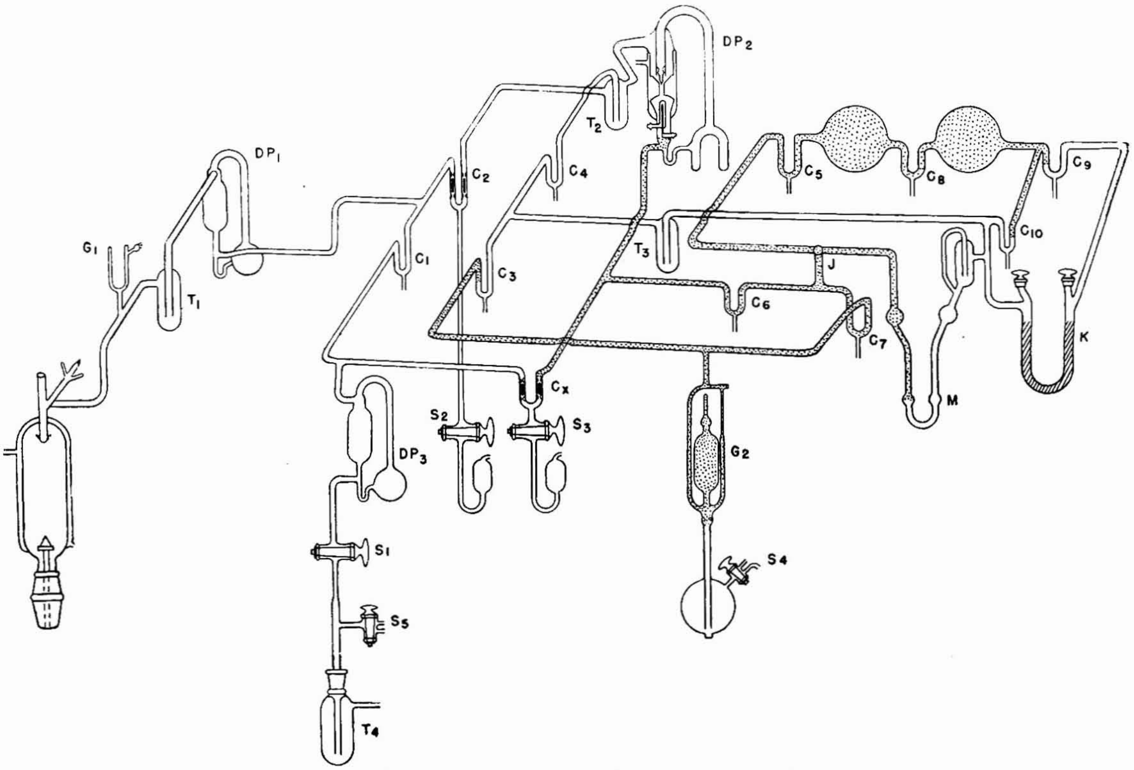

Figure 2. Schematic Diagram of Vacuum Fusion Apparatus

Table II. Analysis of Titanium Standards

(Tin fusion)

Sample No.	Sample Weight	Oxygen Added	Oxygen Recovered
	Gram	%	%
5	0.636	0.32	0.31
6	0.205	0.27	0.27
7	0.534	0.105	0.106
8	0.616	0.065	0.065

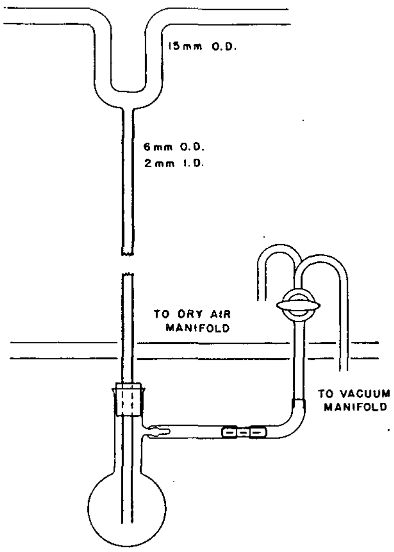

Figure 3. Mercury Cutoff

from the fore pump. The cutoff construction is illustrated in Figure 3. For ease of support and assembly the mercury reservoirs are located in a common well below the table top. They rest in adjustable supporting rings and can be removed or adjusted individually. The control stopcocks are located in a row, near the front of the table, and all manipulations of the cutoff system can be made from one position. Two cutoffs, equipped with floating check valves, C_2 and C_x (Figure 2), are used in the system to make possible the maintenance of high vacuum conditions in the analytical system, while the furnace system is open to the atmosphere.

Furnace System. Guldner and Beach of the Bell Telephone Research Laboratories recently inaugurated the use of an all-glass furnace for vacuum fusion work, in which a quartz tube, suspended from the top of the furnace by platinum wires, is used as a supporting device for the graphite reaction crucible (*5*). This convenient arrangement, which provides full visibility and eliminates metal heads, has been incorporated in the furnace assembly illustrated in Figure 4. The Guldner-Beach furnace is entirely air-cooled.

For the work described here a water-jacketed furnace tube is used. It consists of a water-cooled borosilicate glass cylinder, 7.5 cm. (3 inches) in inside diameter, equipped with a 71/60 standard-taper, ground-glass joint at the bottom. A 1-inch tube leading through the top of the cylinder serves as an exhaust tube for the furnace gases and a delivery tube for admitting the samples and provides an optical path for making temperature observations. Three side arms are sealed onto this vertical tube several inches above the furnace jacket. One arm is connected through diffusion pump DP_1 to the vacuum system; one accommodates a small iron armature, used for manipulating the crucible cover, described below; the third is used for storing samples to be analyzed. The sample loading arm and the one holding the armature are equipped with removable caps made from 29/42 standard-taper joints. The vertical tube extends to a height of 12 inches above the furnace jacket and is capped with 29/42 standard-taper joint assembly into which an optical window is sealed. The window is thus easily removed for cleaning and a port is provided that simplifies cleaning of the furnace tubes.

The quartz tube is 6.5 inches in over-all length and is 2 inches in outside diameter. Two small holes near the open end of the tube are provided to accommodate 0.05-inch platinum supporting wires. The graphite crucibles are made from 1-inch graphite rods, Acheson AGX grade, and are $^{7}/_{8}$ inch in outside diameter, $^{5}/_{8}$ inch in inside diameter, and 2.5 inches long. Thin-walled funnels are machined to fit snugly into the mount of the crucible. The insulating medium which floats the graphite crucible and funnel in the quartz tube is 200-mesh graphite powder (*5*). The crucible is one fourth filled with 20-mesh graphite powder. Both powders are obtained by screening the millings formed in the preparation of the crucibles and funnels.

A loose-fitting graphite cover in the mouth of the funnel serves to prevent the contents of the crucible from being ejected during outgassing operations and minimizes heat losses from the open end of the crucible. The cover is machined from a graphite rod to the shape of a nipple, as illustrated in Figure 4. A small hole is drilled through the length of the rod to permit an easier escape of the furnace gases. The cover is equipped with a bail made from 0.03-inch tantalum wire to which a thin molybdenum wire is attached. The molybdenum wire extends through the exhaust tube at the top of the furnace and is attached to a soft iron armature resting on one of the side arms. The armature can be moved back and forth in the side arm by means of a small Alnico magnet, thus raising and lowering the cover in the mouth of the funnel. Because the pull of the molybdenum wire is slightly off center, the cover is pulled to the side sufficiently far to make optical pyrometer readings possible. An Alundum heat shield is fitted into the top of the quartz tube and is held in place by the same wires that support the tube. In the course of operations the shield becomes coated with tin, and it exhibits no tendencies to evolve or absorb gases.

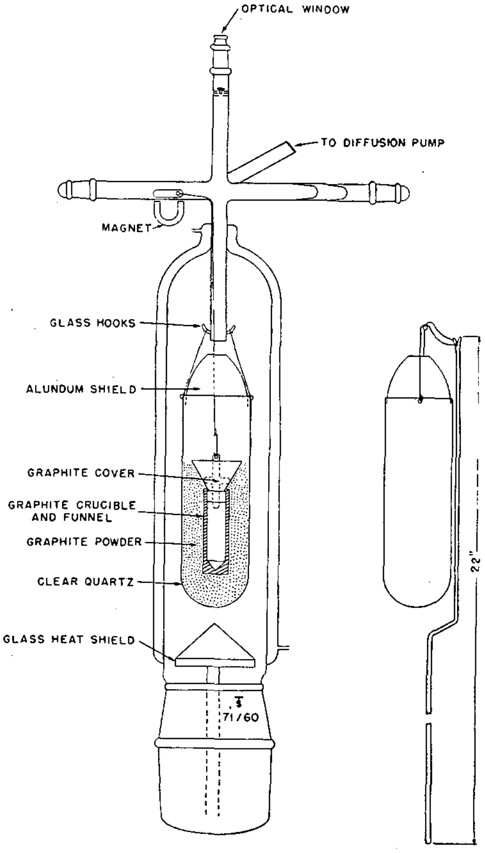

Figure 4. Details of Furnace Design

The completely fitted quartz tube is relatively inexpensive and fairly simple to assemble, so that a number of them can be kept on hand, ready to be placed in service at any time. The time required for removing the tube from the furnace and replacing it with another can thereby be reduced to less than 15 minutes.

The quartz tube assembly is inserted into the furnace tube through the joint at the bottom of the furnace. To eliminate the possibility of scratching the ground surface of the inner joint, a paper sleeve is used for protection. A convenient hook for supporting the quartz tube assembly and inserting it in the furnace is shown to the right of the furnace diagram in Figure 4.

The optical window becomes coated with a thin film of metal in spite of all precautions, but a series of baffle plates, located directly below the window and held in place with a nickel-plated spiral spring, tends to minimize this difficulty. A magnetically operated shutter closes the optical path through the baffle plates except when a temperature reading is to be made.

The sample loading arm has four small side arms for storing samples to be analyzed. An iron pusher is enclosed for moving the nonmagnetic titanium samples into position for dropping into the furnace. The pusher is wrapped in a thin sheet of tin foil to minimize the possibility of sharp, shattering impacts of the hard metal against the glass. A mercury lift for introducing samples under vacuum can be easily attached to one of the small arms, if the need for one should arise (*4*). An ionization gage, G_1, having an effective range of 10^{-3} to 10^{-7} mm., is located on the exhaust tube between the furnace and diffusion pump DP_1. This gage is intended primarily for fractional evolution studies, but it also serves nicely to indicate the general state of furnace conditions.

Diffusion pumps DP_1 and DP_3 are single-stage, high-speed mercury pumps and are operated in series for extracting the furnace gases during preliminary outgassing operations. The diffusion pumps are heated electrically, the power input being indicated by wattmeters and controlled by Variacs. The electrical circuit for the diffusion pumps is connected to the power line through an automatic water pressure switch, which breaks the circuit when the water pressure falls below a safe figure. A cold trap, T_1, is located between the furnace and DP_1 to prevent backstreaming of mercury vapor. All precautions are taken to avoid the hazard of having a mercury globule fall into the hot graphite of the furnace assembly.

Power Supply. The graphite crucible is heated inductively. A tube-driven high-frequency oscillator, which has a power input of approximately 20 kw., provides an easily controlled power output which is more than ample for the heating requirements. The induction coil, which surrounds the furnace tube, consists of twelve turns of $^5/_{16}$-inch copper tubing, flattened to 0.25 inch; the inside diameter of the coil and the over-all height of the coil are both 4 inches. The coil is connected to the oscillator through 8-foot, water-cooled, flexible leads, spaced 4 inches apart. The coil is mounted on a vertical polystyrene support stand.

Analytical System. The portion of the apparatus to the right of C_2 and C_x (Figure 2) constitutes the analytical system. Cutoffs C_2 and C_x are of the special design previously described and are used for maintaining the analytical system at high vacuum when the furnace is opened for recharging.

A two-stage mercury diffusion pump, DP_2, constructed after the design of Naughton and Uhlig (*7*), is used to collect and circulate the gases to be analyzed. The gases are collected in one of the three calibrated volumes. The largest volume is 2755 ml. and is represented by the shaded area in Figure 2. The volume can be confined to 1730 ml. by closing C_8 or to 680 ml. by closing C_5. The McLeod gage, G_2, is always part of the calibrated volume, and it is used for making all pressure measurements during the course of an analysis. The range of the gage is 0 to 1700 microns; the most accurate range lies between 0 and 175 microns. When gases are being collected, the calibrated volume is so chosen that the final pressure of the gases is less than 175 microns, if possible. The gage is joined to the system on both sides of DP_2, which makes it possible to evacuate the gage during the circulation of the gases over the catalyst. A manometer, *M*, also ties into the system and is used to give a rough indication of the pressure. It is a magnified deflection-type manometer, having mercury in the arm that is open to the calibrated volume and Amoil-S in the other (*4*).

The catalyst in *K*, used for oxidizing the hydrogen to water vapor and the carbon monoxide to the dioxide, is a mixture of cupric oxide, rare earth oxides, and kaolin (catalyst used by Bureau of Standards in vacuum fusion work). It is prepared by dissolving 150 grams of pure copper and 23.5 grams of rare earth oxides in nitric acid. (The rare earth oxides should have a cerium content not less than 35%.) The two solutions are mixed and evaporated to dryness. The dry mixture is heated to drive off the acid fumes and then brought to a temperature of 800° C. and maintained there for 24 hours. The ignited mixture is crushed and put through an 80-mesh screen, mixed with 36 grams of pure kaolin, and moistened with water to form a plastic mass. This mixture is dried and baked at 800° C. for 4 hours, after which it is broken into small lumps and reduced in a stream of hydrogen at a temperature of 300° to 400° C. It is reoxidized at the same temperature. The process of reduction and oxidation is repeated. After the final oxidation, the material is crushed and put through a 10-mesh screen. The material retained on a 20-mesh screen is placed in the catalyst U-tube, *K*.

The catalyst tube is maintained at a temperature of 325° C. by means of a small, electrically heated pot-type furnace. Provision has been made at the extremities of the U-tube for removing the catalyst for reactivation. The same catalyst has been used in this apparatus for over a year, however, without the need of reactivation and without evidence of loss of efficiency.

Trap T_3 is used for separating the oxidation products of the catalysis by differential freezing. A dry ice–acetone mixture, supercooled to −95° C. by subjecting it to reduced pressure, is used for freezing out the water vapor. Liquid nitrogen (−195° C.) is used for freezing out the carbon dioxide.

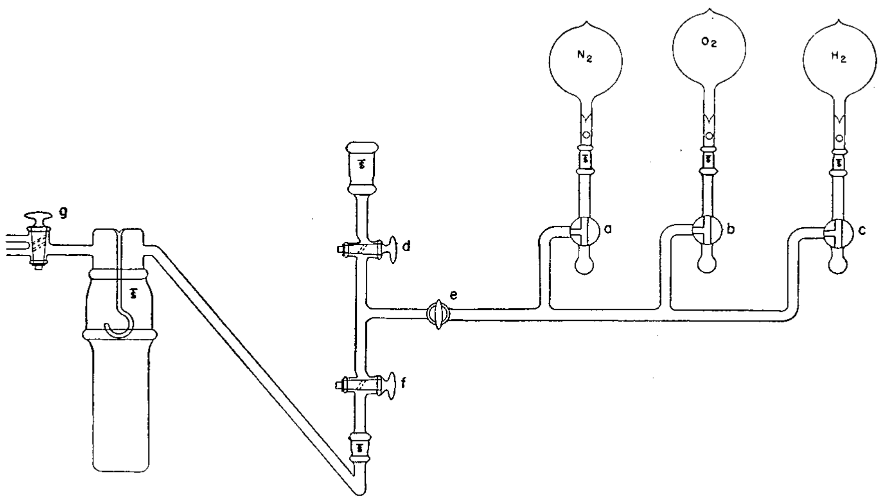

Figure 5. Gas Addition Apparatus

At junction *J*, a 29/42 standard-taper joint is provided for attaching a small calibrated volume to the analytical system. This small volume is used for calibrating the analytical system originally and for recalibration in the event changes are made in the system which affect the volume. It is at this point also that the apparatus used for the preparation of standard samples, described below, is joined to the system.

STANDARDIZATION

The lack of titanium metal of known oxygen content made it necessary to prepare standards which would simulate as nearly as possible the actual conditions of combination encountered in analytical investigations. Titanium metal, prepared by the thermal decomposition of the tetraiodide, was chosen as the base metal to which additions of oxygen would be made.

Gas Addition Apparatus. The apparatus illustrated in Figure 5 provides for the addition of nitrogen, oxygen, and hydrogen to metal samples. Three 1-liter flasks of the pure gases (99%+) are connected by means of standard-taper joints, through three-way T-bore stopcocks, *a*, *b*, and *c*, to a common manifold. One arm of each stopcock is sealed off, as illustrated, to provide a volume of approximately 0.5 ml. A small steel ball is placed in the neck of each flask for breaking the glass seal. An absorption chamber (extreme left in Figure 5), 1.25 inches in outside diameter and 8 inches long, is connected to the apparatus by means of a 34/45 standard-taper joint. The outer joint constitutes the head of the absorption chamber, and it is equipped with a glass hook, from which samples are suspended; a three-way capillary stopcock, *g*, for bleeding gas into the system and for the initial evacuation of the system; and a connecting tube for joining the absorption chamber to the gas manifold. Three stopcocks, *d*, *e*, and *f*, are placed as illustrated to provide for versatile handling of the addition gases.

The addition apparatus is connected to the analytical system at point J (Figure 2) by means of a 29/42 standard-taper joint. The volume of the addition apparatus represented by the area to the left of stopcock e (Figure 5) and below stopcock d is 175 ml. By adding this volume to the calibrated volume of the analytical system, the addition gases are measured in the same volumes and with the same gage which are used later for measuring the gases evolved in the course of the analysis. This procedure cancels any slight errors which may exist in the calibration of the gas volumes and the basic accuracy of the McLeod gage.

Preparing Standard Samples. With the addition apparatus connected to the analytical system, the analytical system maintained at high vacuum and stopcock d closed, a piece of titanium metal, prepared by the iodide method and weighing about 0.5 gram, is attached to a piece of thin platinum wire. The wire is attached to the glass hook in the chamber head so that the titanium sample will be suspended near the middle of the chamber. The apparatus is assembled and evacuation is begun through stopcock g, with the larger mechanical pump. When the pressure is reduced to the ultimate obtainable with the mechanical pump, the addition system is opened to the analytical system and evacuation is continued, with diffusion pumps DP_2 and DP_3. When a pressure of the order of 10^{-4} mm. is reached, the titanium sample is heated inductively, with a small spark-gap, high-frequency generator, having a power input of 3 kw. This drives off the hydrogen contained in the sample, which is exhausted through the pumping system.

When the hydrogen is driven off, the sample is allowed to cool, and cutoffs C_3, C_5, and C_6 are closed. A volume of oxygen is admitted to the system from the oxygen flask through stopcock b, and the pressure is measured on the McLeod gage. If a smaller amount of oxygen is desired, C_6 is opened for a moment, permitting the excess to be pumped off. If a larger amount is desired, another volume is admitted through b. When the desired quantity is obtained, e is closed. This gives an exact volume of 630 ml. of gas available for addition to the sample.

The titanium sample is heated again to the maximum temperature obtainable (about 1100° C. with this power unit). The oxygen pickup begins well below this temperature, however, and at temperatures above 1000° C. the pickup is almost instantaneous for the small amount of oxygen involved. The temperature is maintained at a maximum for 15 minutes after the pickup is complete to give the oxygen opportunity to diffuse into the metal and attain homogeneity. If the addition temperature is much below 1000° C., the pickup is slow and the diffusion of the oxygen into the titanium is not complete, as indicated by discoloration of the metal surface. After the diffusion period, the power is turned off, the sample permitted to cool, and the residual pressure measured. Nitrogen, if desired, is added similarly. Hydrogen is added at much lower temperatures (approximately 300° C.).

When the gas additions have been made, dry helium is admitted to the addition system, and the sample is removed. A piece of titanium metal, cut from the same stock as that used for the preparation of standards, is always analyzed with the standards as a blank.

ANALYTICAL PROCEDURE

Preparation of Sample. A solid piece of titanium is cut from the stock metal in such a way as to obtain a section that is representative of the whole cross section. The cutting is done slowly enough to keep the heating of the sample to a minimum, preferably with a jeweler's saw. The samples are washed in carbon tetrachloride. The weight of the samples should fall between 0.2 and 0.5 gram, and a piece of clean stick tin, having a weight approximately twice that of the titanium, is provided for each sample. The titanium-tin sample pairs are pressed together until they adhere sufficiently to be handled as one sample. If small pieces of titanium or powdered titanium are to be analyzed, the sample is wrapped in bright tin foil of the appropriate weight. Tin foil is more convenient to use than stick tin, but the blanks run slightly higher because of the greater surface area.

Preparation of the System. With the furnace and analytical systems outgassed and static conditions being maintained throughout, the procedure is as follows:

Cutoffs C_2 and C_x are closed and the control stopcocks, S_2 and S_3, are turned to the cutoff position, thus isolating the furnace from the analytical system. Cutoff C_1 is opened, and helium is admitted to the furnace system through S_5. The mercury column below the U-tube of C_1 serves as a manometer, indicating the pressure within the system. After the pressure rises to atmospheric, the ground-glass plug at the bottom of the furnace tube is removed and the quartz tube assembly is extracted, using the forked rod illustrated in Figure 4, and a freshly assembled quartz tube is inserted.

The optical window is cleaned, the samples to be analyzed are loaded in the appropriate side arm in the order in which they are to be analyzed, the pusher is enclosed, and the system is again sealed.

The small mechanical pump is started and by proper manipulation of the valves of the pumping system, evacuation is begun through S_5. This permits slow pumping, thus preventing the fine insulating powder from being disturbed and gives the operator an opportunity to seat the glass joints properly. Again the mercury column of C_1 serves as a manometer and indicates the progress of the evacuation. When the pressure drops to a few centimeters of mercury, the large mechanical pump is started and S_5 is closed.

Outgassing. When the pressure within the furnace system drops to a few microns, the diffusion pumps are started. Dry ice–acetone mixtures are placed around T_1 and T_4. With the diffusion pumps operating at their maximum pumping speed, the high-frequency oscillator is started and the heating of the crucible is begun. The heating is done slowly at first, until the major volume of the easily liberated gases is extracted and the graphite powder within the crucible no longer has a tendency to be ejected. The temperature is then allowed to rise slowly until a crucible temperature of 2300° to 2400° C. is reached. This temperature is maintained for 4 hours or until such a time as blank conditions are favorable, as described below.

While the outgassing is in process, DP_2 is started and the catalyst is brought up to temperature (325° C.). A small amount of gas evolves from the catalyst while it is being heated and is pumped off continuously by operating DP_2 with C_3 and C_6 closed and C_x open.

Determining the Blank. The ionization gage is used to indicate the progress of the outgassing operation. When the gage shows that the pressure has been reduced to the 10^{-4} mm. range, with a crucible temperature of 2300° C., a blank is collected as follows:

The temperature is dropped to 1900° C. After a few minutes have elapsed, the furnace gases are collected for a 15-minute period in the volume represented by the shaded area in Figure 2. Unless analyses of unusual accuracy are to be made, a total blank of 5 microns per 15-minute period is satisfactory. The carbon monoxide usually constitutes about one third of the total gas collected, which represents a blank of approximately 0.025 ml. (N.T.P.) of carbon monoxide per hour at the above rate.

The first blank collected is measured and pumped out of the system without being analyzed. If it indicates that conditions are satisfactory for the beginning of the analytical work, the temperature is lowered to 1200° C., and a 2-gram piece of tin is dropped into the crucible. The temperature is then raised slowly until the activity of the tin-graphite mixture subsides, after which the temperature is allowed to rise to 2000° C. This first charge of tin is necessary to condition the crucible and to obtain a blank under operating conditions.

The blank to be applied in the analysis of a piece of titanium metal is collected over the same temperature cycle used in the course of an analysis. Normally, the initial crucible temperature is 1200° C., rising to 1900° C. at the end of the run, the total time being 30 to 40 minutes. The blank gases are separated by differential freezing.

Analysis of Sample. After the crucible has been conditioned with tin and a satisfactory blank has been collected and analyzed, the analytical system is pumped down to 10^{-4} mm. (Any initial pressure less than 1 micron is negligible, for it is impossible to read the final pressure of the collected gases closer than ± 1 micron.) The cutoffs are in the same position as specified for the collection of the blank, the temperature is lowered to 1200° C., and a piece of titanium is dropped into the furnace along with a piece of tin. The cover of the crucible is raised slightly to permit the metals to drop into the crucible and then is replaced. The power is turned on with the controls set to give a maximum temperature of 1900° C. Pressure measurements are made every 2 minutes with the McLeod gage to follow the progress of the evolution. All of the hydrogen is evolved by the end of the first 2 minutes, after which there is no further evolution of gas until a crucible temperature in the 1700° C. range is reached.

From observations made of the reactions when no tin was present in the crucible, the titanium carbide is formed exothermically at about 1650° C., and the carbon monoxide begins to evolve at about 1750° C. In the presence of tin, however, the temperatures at which the reactions take place are more difficult to observe. The temperature at which carbon monoxide begins to evolve is somewhat lower when tin is present, but it is still several hundred degrees above the temperature at which the hydrogen evolution is complete. Analysis shows that little or no nitrogen is evolved from the titanium sample under these conditions. Some of the graphite powder may be ejected from the crucible in spite of the cover, so it is necessary occasionally to raise the cover slightly to permit the powder to fall back into the crucible. The heating is continued until the rate of increase in pressure is equivalent to the blank.

At this point, C_2 is closed, C_1 is opened, and the furnace temperature is raised several hundred degrees and maintained there for 10 minutes in preparation for the next sample. During this period, this analysis of the collected gases is begun. A reasonably accurate estimate of the hydrogen and oxygen content of a sample can be made without analyzing the gases, by observing the amount of each gas evolved in its characteristic temperature range during the heating cycle. For most accurate work, however, the gases are separated by differential freezing, after circulating over the catalyst.

If the amount of gases collected from a sample is large, the analysis can be conducted more quickly and more accurately on an aliquot. This is taken by closing cutoffs C_8, C_9, and C_{10}, thus entrapping about one-third of the total gas volume. After the other fraction is pumped out of the system, the aliquot is expanded into the total calibrated volume, measured on the McLeod gage, and analyzed.

An analysis is always run on the tin used for fluxing. The amount of hydrogen and oxygen is usually small, if clean tin is used, but for a high degree of accuracy and precision, this analysis, plus the analysis of the blank furnace gases, is applied as a correction against the analysis of each titanium sample.

As many as five samples have been run in the same crucible with one charge of graphite powder. The crucible can be cleaned upon removal from the furnace and reused, because there is very little attack on the crucible walls.

ACCURACY AND REPRODUCIBILITY OF METHOD

Table I shows the oxygen recovery on a series of standards when no tin was used to alloy with the titanium. The sample weight is approximately the same in each case, whereas the amount of oxygen varies. The fraction of oxygen recovered is nearly the same for each sample, although it is only about 90% of the amount added.

Table II shows the oxygen recovered on a series of standards when tin was used to alloy with the titanium. No attempt was made to correlate sample weight and oxygen concentration. By this method the recovery is practically complete. Sample 6 was prepared by making an addition of spectrographically pure titanium dioxide to titanium metal; all others were prepared by making gaseous additions to the hot metal.

Table III shows the reproducibility that is obtainable. The analyses were made on titanium samples prepared by different commercial processes. The series serves to illustrate also the range of oxygen concentrations which may be expected in analytical work and gives some indication of the pickup tendencies of the metal during fabrication. No other oxygen analyses were available on these samples from other sources for comparative studies.

Samples 9 through 12 were taken from different sections of a large titanium filament, prepared by the thermal decomposition of the iodide. No. 13 was 0.04-inch wire drawn from the same stock, and shows a pickup of about 0.01%. Sample 14 was untreated sponge. Samples 15 and 16 were taken from the same stock as No. 14 and heated in different zones of a vacuum annealing furnace. Sample 17 was taken from the same stock as No. 14 and melted in argon. Sample 17 also contained a considerable amount of hydrogen, indicating that there was probably water vapor present in the argon. Samples 18 through 21 were taken from small ingots, prepared by arc-melting sponge in high vacuum.

LIMITATIONS OF METHOD

It is impossible to determine the lower limit of oxygen concentrations detectable by this method, inasmuch as the most nearly oxygen-free titanium obtained to date has analyzed 0.006%. If there is a residual quantity of oxygen that is not evolved, it escapes the present methods of detection. No attempt has been made to establish an upper limit of oxygen concentration that can be determined with accuracy. For the present work, an upper limit of 0.5% has provided a safe margin, and standardization work was not carried beyond that order of concentration.

Table III. Analysis of Various Types of Titanium Metal

Sample No.	Sample Weight *Gram*	Method of Preparation	Form of Sample	Oxygen Analysis %
9	0.369	Iodide	Solid	0.011
	0.349			0.011
10	0.690	Iodide	Solid	0.007
	0.627			0.011
	0.690			0.012
11	0.569	Iodide	Solid	0.006
	0.603			0.005
12	0.300	Iodide	Solid	0.014
	0.275			0.015
13	0.247	Iodide	Wire	0.021
	0.416			0.021
	0.367			0.019
14	0.330	Reduction	Sponge	0.128
	0.542			0.132
15	0.434	Reduction	Sponge vacuum annealed	0.175
	0.419			0.160
16	0.433	Reduction	Sponge vacuum annealed	0.152
	0.391			0.144
17	0.344	Reduction	Sponge melted in argon	0.31
	0.371			0.29
18	0.372	Reduction	Solid	0.117
	0.450			0.118
19	0.640	Reduction	Solid	0.118
	0.321			0.119
20	0.550	Reduction	Solid	0.094
	0.547			0.096
21	0.663	Reduction	Solid	0.129
	0.471			0.122

CONCLUSIONS

A method has been developed for the determination of oxygen in titanium which yields analyses of satisfactory accuracy and precision. It eliminates the use of troublesome metal baths, with a resulting longer life for crucibles, and provides for simplicity in the analysis of the evolved gases. Conventional vacuum fusion equipment can be adapted to utilize the method with only minor modifications. The method provides a foundation for further oxygen-titanium investigations.

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Quantitative Techniques with Carbon 14

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Experimental methods are described which have been developed for use with small amounts of carbon 14 labeled compounds of high specific activity. Techniques are presented for establishing the relationship of weight to radioactivity using 3 to 15 micrograms of the labeled compound, preparing carbonate samples for counting, and using infrared spectrophotometry for the determination of chemical purity of carbon 14 compounds.

MUCH of the research with radioisotopes as tracers has had as its aim qualitative information concerning the fate of labeled atoms in chemical or biological systems. The extreme sensitivity of the method of measurement makes it possible to utilize radioisotopes also as a quantitative analytical tool. Carbon 14 is being used by a number of laboratories as a method of analysis for very small amounts of labeled compounds in the products of complicated reactions.

In order to carry out quantitative measurements it is necessary to establish the relationship between weight of the labeled material and its radioactivity. The best method of determining this relationship depends upon the procedure for counting and the compound to be assayed. Because of the self-absorption of the low-energy beta-ray of carbon 14 it has been the practice to count all samples as a reproducible solid, such as barium carbonate, or in the gas phase as carbon dioxide. If the labeled material to be assayed is a uniform solid, a small amount can be weighed to the desired accuracy and converted to the counting compound and its radioactivity can be measured in the same way in which the product materials will be assayed. Greater difficulties are encountered when the labeled compound is of high specific activity, when even a few milligrams can represent 10 to 100 microcuries. It is not advisable to handle samples of this activity in the same apparatus that will be used later for analytical samples containing activity on the order of background. Gaseous or volatile compounds are difficult to sample by direct weighing.

APPARATUS FOR ALIQUOTING MICROGRAM SAMPLES OF VAPOR

An apparatus is described here for sampling gaseous or volatile compounds of high specific activity, using a closed glass system which facilitates handling without exposure of the material to the atmosphere.

By use of a vacuum manifold a known small volume of the gas or vapor is isolated at low pressure, distilled into a glass ampoule, and sealed with a flame. The ampoule can then be introduced into a combustion tube and the gas burned to carbon dioxide. By using an all-glass vacuum system, which can be flamed between exposures to the radioactive material, and a small volume (this was 0.1467 ml.) it is possible to measure out amounts of the compound on the order 3 to 15 micrograms with an accuracy of ±1 to 2%.

EXPERIMENTAL

The apparatus is diagramed in Figure 1.

The labeled compound is put on the vacuum manifold at *A* in a glass ampoule with a break-seal and ground joint. The system is pumped thoroughly and outgassed with a Bunsen flame. The mercury is allowed to rise in the cutoff, *M*, which is made of 1.25-cm. (0.5-inch) diameter barometer tubing and stopcock *D* is closed. The seal is broken on the sample ampoule with the steel projectile and the active compound is distilled into *B* with liquid nitrogen. The mercury in *M* is lowered and the pressure is read on the thermocouple gage, *TC*. Any noncondensable gases can be pumped away while holding the sample at liquid nitrogen temperature in *B*. The glass system to the right of *M* is again flamed and pumped. Then with *D* closed the liquid nitrogen at *B* is replaced by a bath at a temperature to give a vapor pressure within the range of the manometer, *M*. The mercury is raised in *M* and the sample is again frozen with liquid nitrogen.

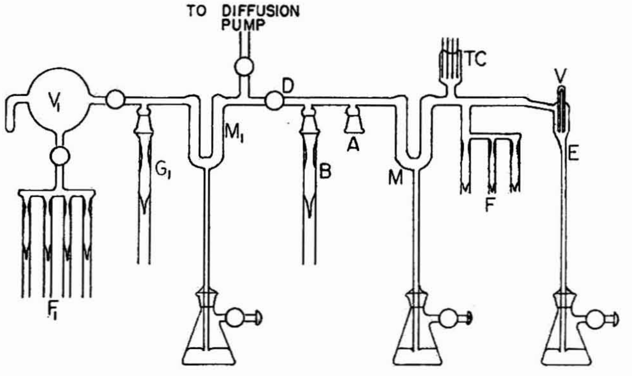

Figure 1. Diagram of Apparatus

The mercury is raised in tube *E* to a point just a fraction of a millimeter below the opening of the known volume, *V*. The pressure to the left of *M* is the vapor pressure of the sample at liquid nitrogen temperature and the difference in the height of the mercury on the two sides of *M* is measured by a cathetometer after temperature equilibrium is established. The temperature is measured with an external thermometer. The mercury is raised in *E* until the level is well above the opening of *V*. This isolates the volume of gas *V* at the measured temperature and pressure. *M* is opened and the gas in the sampling system is frozen into *B* again, keeping *V* isolated with the mercury.

The system is again flamed and pumped until the thermocouple gage shows its ultimate pressure reading, indicating a pressure lower than 0.5 micron. The mercury is again raised in *M* and then communication between volume *V* and the system to the right of *M* is made by lowering the mercury column in *E*. The gas from *V* is distilled into one of the ampoules, *F*, with liquid nitrogen and the system is flamed. The thermocouple gage indicates

Table I. Sampling High Activity Carbon Tetrachloride

Aliquot		Pressure	Temp.	Calcd. Wt. of Aliquot	Wt. of $BaCO_3$	Sample Carbon in 1 G. $BaCO_3$	Deviation from Average
		Mm.	° *C.*	γ	*Gram*	*Counts/min./γ*	%
CCl_4	1-1	10.15	24.4	12.34	0.1455	521.8	−0.1
	1-2	10.47	25.5	12.69	0.1532	530.6	+1.5
	1-3	10.57	25.7	12.80	0.1450	514.9	−1.5
CCl_4	2-1	9.01	25.2	10.93	0.1493	341.0	+0.6
	2-2	9.01	25.7	10.91	0.1528	336.0	−0.9
	2-3	9.15	25.7	11.08	0.1476	340.2	+0.3
CCl_4	3-1	9.58	30.3	11.43	0.1597	538.2	0.0
	3-2	12.50	30.1	14.91	0.1533	529.6	−1.6
	3-3	8.95	30.5	10.44	0.1486	546.6	+1.4
CCl_4	4-1	9.25	26.4	11.18	0.1094[a]	333.1[a]	−1.0
	4-2	11.40	26.2	13.78	0.1096	335.4	−0.3
	4-3	9.37	26.2	11.32	0.1152	341.1	+1.4
CO_2	4-1	11.63	25.0	4.03	0.1133	354.2	−0.9
	4-2	12.10	25.0	4.20	0.1142	348.2	−2.6
	4-3	10.30	25.0	3.57	0.1152	370.3	+3.6

[a] $CaCO_3$ used as counting solid for CCl_4 4 and CO_2 4.

when all the gas has been driven into the ampoule, which is then sealed off from the system. Repetition of this procedure allows as as many samples to be taken as desired.

The same technique is used to meter out samples of known weight for use in tracer experiments.

The labeled compound is transferred to tube G_1 after the system to the left of the pumping lead on Figure 1 has been thoroughly evacuated. The known volume, V_1, and the manometer cutoff, M_1, are used. The metered samples are frozen into the ampoules, F_1, and sealed off. The flaming of the system can be eliminated here because the size of the metered samples is on the order of 10^3 to 10^4 times that of the samples taken for analysis. The active material remaining after the required samples are taken can be frozen into the bottom of G_1 and sealed off.

The combustions are carried out in a semimicro combustion tube packed with copper oxide, platinized asbestos, and silver wool in the form of a "simple band" filling (*3*). Because the amount of carbon dioxide from the microgram samples is very small, some inactive compound is burned after the active material to give a weighable amount of carbonate and to flush the combustion tube to ensure complete collection of the radioactive carbon dioxide. A weighed sample of pure benzoic acid, enough to give about 120 mg. of carbonate, is placed in a platinum boat and put into the sample position. The ampoule is cooled in liquid nitrogen, the seal is broken with a glass rod, and the ampoule is quickly pushed into the combustion tube behind the benzoic acid on a platinum foil, so that the radioactive sample is burned first. Uniform rates of burning are achieved by using a motor-driven furnace at 750° C. The carbon is burned in a stream of pure oxygen of 12 to 14 ml. per minute. The combustion tube is swept with 250 ml. of oxygen and the carbon dioxide is absorbed in a fivefold excess of 1 *N* carbonate-free sodium hydroxide. The carbonate is precipitated with barium or calcium chloride and the solid is deposited as a uniform layer on an aluminum counting plate (*2*, *5*).

These plates are kept and used as counting standards throughout the experiments in which the radioactive compound is used. These standards permit a day-to-day check on the changes in efficiency of the Geiger tube for carbon 14 radiation, which can be considerably different from changes in efficiency for harder radiation such as is provided by RaD + E standards. The counting results given here are for "thick" layers—i.e., greater than 20 mg. per sq. cm. Data for sampling high activity carbon tetrachloride are given in Table I.

The absorption of the carbon dioxide as soluble sodium carbonate allows the precipitation of an insoluble carbonate uniform with respect to carbon 14. A combustion procedure which absorbs the carbon dioxide in calcium or barium hydroxide produces a precipitate which is inhomogeneous in radioactive carbon and may produce counting errors due to self-absorption of the beta-rays. This also holds where biological samples are burned, inasmuch as the combustion rate of the carbon 14 compounds in the sample may not be the same as that of all the other compounds present and a fractionation may occur during the combustion which will produce erroneous counting analyses.

Several attempts have been made to obtain an accurate ratio of weight to counts per minute on Oak Ridge barium carbonate in which 5.9% of the carbon is radioactive. The results are not reproducible, presumably because of nonuniformity of the barium carbonate.

In these experiments a small amount, on the order of 0.5 to 1 mg., of the carbonate was accurately weighed on a microbalance and dissolved in water in a volumetric flask. The solubility of barium carbonate is 2 mg. per 100 ml. of water at 18°. An aliquot of this solution was pipetted into a precipitation flask along with 25 ml. of a standard sodium carbonate solution of concentration to give 111.8 mg. of calcium carbonate. This calcium carbonate was counted as a thick sample. Results are given in Table II.

Duplicate precipitations from the same $BaC^{14}O_3$ solution gave excellent checks; the counts agreed within less than 1%, the statistical counting error.

This nonuniformity could be overcome by evolving carbon dioxide from the carbonate, absorbing it in alkali, and reprecipitating the carbonate.

The barium carbonate used here (238 mg.) was diluted with 268 mg. of ordinary barium carbonate and sampled in the gas-sampling apparatus as CO_2 4 in Table I. To compare the average value of column 5, Table II, with the average value of column 6, Table I, for CO_2 4 it is necessary to multiply by the dilution factor 238/(238 + 268). The carbon 14 assays obtained from the two

Table II. Count of Barium Carbonate

Run No.	Wt. of $BaC^{14}O_3$	Wt. of Aliquot	Background	Sample Carbon in 1 G. $CaCO_3$	Deviation from Mean
	Mg.	γ	*Counts/min.*	*Counts/min./γ*	%
1	0.546	5.46	1955	657.1	−7.0
2	0.320	4.00	1708	783.7	+10.7
3	0.888	4.44	1624	671.7	−5.0
4	0.637	3.18	1230	710.3	+0.3

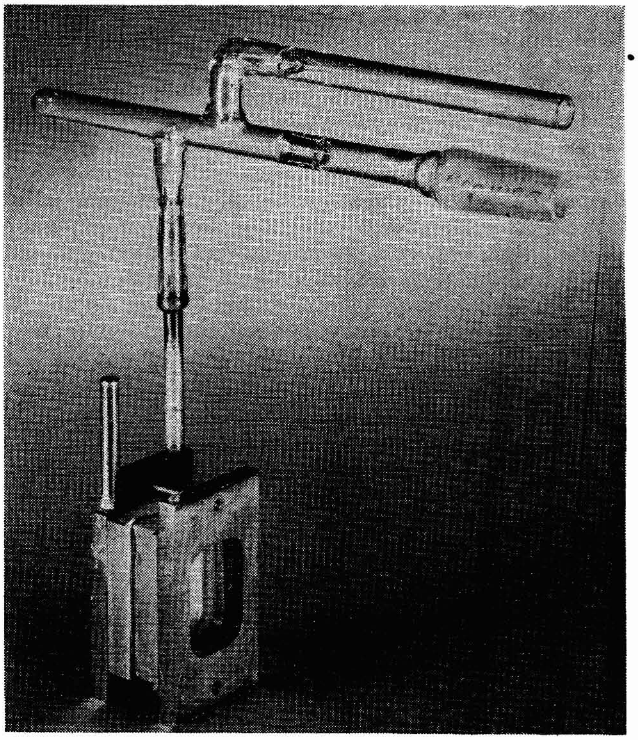

Figure 2. Cell

methods differ by 7%, which is about the experimental error of the data of Table II.

The CCl_4 4 sample in Table I was synthesized from CO_2 4 (*1*). The value obtained in column 6 for the carbon tetrachloride is about 6% lower than for the carbon dioxide from which it was synthesized. Because the specific activity of the compounds is very high and the total amount is only 2.5 millimoles, less than 2 mg. of ordinary carbon picked up during the synthesis would account for this drop in specific activity.

PREPARATION OF CARBONATES

The precipitation of barium or calcium carbonate from the alkaline absorption solution must be carried out with good analytical technique if one is to avoid errors due to coprecipitation of the hydroxides. Adding the barium or calcium solution directly to the alkaline carbonate solution can give positive errors of 2 to 5% even when the hydroxyl ion concentration has been lowered by the addition of the equivalent amount of ammonium chloride. This error can be reduced to less than 1% by diluting the carbonate to about 150 ml., adding an amount of ammonium chloride 20% in excess of the sodium hydroxide used in the absorption solution, heating to boiling, and adding a twofold excess of 0.3 *N* barium or calcium chloride dropwise with constant agitation. This procedure reduces the coprecipitation error to within the usual statistical counting error and gives a precipitate which can be easily deposited as a thin, uniform solid layer for counting (*4*).

Table III. Count of Barium and Calcium Carbonates

Aliquot of C 14 Solution	Carbonate	Wt. of Carbonate	Counts/Min.
Ml.		*Mg.*	
5	Ba	232.3	677
5	Ba	232.6	669
5	Ca	118.0	1173
5	Ca	117.6	1160

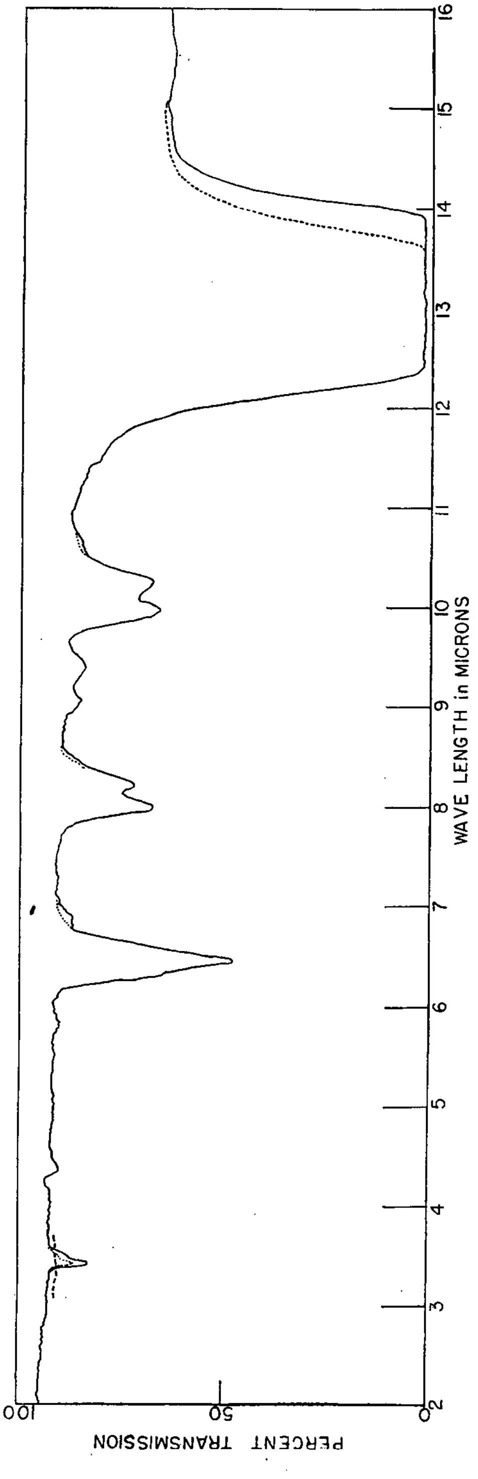

Figure 3. Infrared Spectrum of Carbon Tetrachloride

Calcium carbonate is less soluble than barium carbonate, does not exchange appreciably with the carbon dioxide of the air, and is suitable for making counting plates. The ratio of the weight of carbon to the total weight of carbonate is approximately twice as great for calcium carbonate as for barium carbonate. Thus on samples of low specific activity the calcium carbonate is preferable. This is illustrated by the counting results in Table III, which show the counting rates for thick samples of the two carbonates which contain the same amount of carbon 14.

DETERMINATION OF PURITY

In experiments using a labeled compound as a quantitative analytical tool, small amounts of radioactive impurities can lead to erroneous results, especially if the impurity is selectively taken up in some part of the system being studied. A method of analysis of the radioactive compound is needed which will be applicable to very small amounts of material, permit recovery of the sample, and have due regard for its hazardous nature. In the case of gaseous or volatile compounds it is again necessary to work in a closed system.

Infrared spectrophotometry has proved to be a useful method of analysis which permits fulfillment of these requirements. The cell shown in Figure 2 can be used for volatile liquids.

This vacuum-tight cell with rock salt windows and amalgamated lead gaskets is connected through a Kovar-to-glass seal to a vacuum line. The labeled compound is distilled into the freeze-out tip with liquid nitrogen and the cell with its glass assembly is sealed off from the line at the constriction and removed. The liquid nitrogen is taken away and the liquid is allowed to run into the cell through the metal stem and a hole drilled in one of the rock salt plates. The second stem is not used and is sealed with solder at the bottom. In the cell shown the liquid layer is 0.121 mm. thick. After the spectrum has been run, the cell is connected to the vacuum line by sealing a ground joint to the tube which contains the break seal. The cell is put on the vacuum line and the air is evacuated. The break-seal is opened with an iron weight and the compound is distilled out of the cell into a new ampoule.

Figure 3 shows the infrared spectrum of 300 mg. of carbon 14 tetrachloride containing 5 mc. of carbon 14 superimposed on the spectrum of a pure inactive sample of carbon tetrachloride. The radioactive compound is shown as the solid line, the inactive compound as the dotted line. The spectra were obtained with a Baird Associates double-beam infrared spectrophotometer. The spectra were made using the same cell and the vacuum technique for filling. The samples were quantitatively recovered. At 3.4 microns a small amount of a hydrocarbon impurity appears in both spectra. The dashed line shows the inactive carbon tetrachloride in a different cell. This impurity is present in the records of both the radioactive and inactive compounds and so is not radioactive but is probably distilled by liquid nitrogen from the stopcock grease. The deviation of the two curves which are evident at the right of each deep band is the displacement of the band due to the isotope effect. It is most pronounced in the large band at 13 microns, where the band due to carbon 14 overlaps the normal band and produces broadening. By using a gas cell or a dilute solution of the radioactive carbon tetrachloride in a solvent transparent to the infrared in the 13-micron region, it would be possible to resolve the two bands and obtain a quantitative value for the isotope ratio.

ACKNOWLEDGMENT

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Determination of Chloride

Modification of Volhard Method

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Calculations have indicated and experiments confirmed that stable end points can be obtained in the presence of the silver chloride precipitate when chloride is determined by the Volhard titration, provided the ferric iron concentration is made approximately 0.20 volume formal at the end point. Alternative procedures for the titration have been developed. Confirmatory analyses indicate that an accuracy of ±0.1 mg. of chloride can be attained when the titration is made with 0.1 formal standard solutions and when the final volume of the titrated solution is approximately 100 ml.

THE desirability of having a volumetric method for the determination of chloride in acid solutions has led to the utilization of the original Volhard (*8*) titration of silver. An excess of silver ion is added, and the excess is back-titrated with thiocyanate, ferric iron being used as indicator.

Drechsel (*2*) and later Rosanoff and Hill (*6*) pointed out that this procedure is inaccurate because of the metathesis of the silver chloride to silver thiocyanate which occurs in the vicinity of the end point. Kolthoff and Stenger (*4*) discuss this effect and show calculations indicating that under the usual conditions as regards the concentration of ferric indicator, volume, etc., it will be necessary to add an excess of 1.60 ml. of 0.1 *F* thiocyanate before a permanent end point is obtained; they state that "experimentally it is found that this excess amounts to 2.5 ml. of 0.1 *F* thiocyanate." Various expedients have been used to minimize this effect. Rosanoff and Hill (*6*) recommended that the silver chloride precipitate be filtered before the titration, and Kolthoff and Stenger (*4*) confirm the accuracy of this procedure. In order to obviate the filtration, Rothmund and Burgstaller (*7*) suggested thorough coagulation of the precipitate or the addition of a layer of an organic solvent such as ether; Caldwell and Moyer (*1*) recommended the addition of nitrobenzene and this procedure has been used extensively. However, in none of these latter methods do equilibrium conditions prevail and therefore the procedures have to be closely followed in order to obtain reproducible values.

Advantage does not seem to have been taken of the fact that an increase in the concentration of the ferric ion used as indicator would cause a decrease in both the thiocyanate and chloride ion concentrations at the end point and therefore in the error of the titration under equilibrium conditions. The indicator concentration which would theoretically eliminate this error can be calculated as follows:

For the titration to be free of error, the total equivalents of silver present when the end point is taken should be equal to the sum of the total equivalents of chloride and of thiocyanate present, or

$$\Sigma \text{ equiv. Ag} = \Sigma \text{ equiv. Cl} + \Sigma \text{ equiv. SCN} \qquad (1)$$

At the end point of the titration

$$\Sigma \text{ equiv. Ag} = \text{equiv. AgCl} + \text{equiv. AgSCN} + \text{equiv. Ag}^+ \qquad (2)$$

$$\Sigma \text{ equiv. Cl} = \text{equiv. AgCl} + \text{equiv. Cl}^- \qquad (3)$$

$$\Sigma \text{ equiv. SCN} = \text{equiv. AgSCN} + \text{equiv. SCN}^- + \text{equiv. FeSCN}^{++} \qquad (4)$$

Therefore Equation 1 can be reduced to

$$\text{Equiv. Ag}^+ = \text{equiv. Cl}^- + \text{equiv. SCN}^- + \text{equiv. FeSCN}^{++} \qquad (5)$$

Previous experiments had shown that a perceptible color was obtained upon adding 0.10 ml. of 0.01 volume *F* potassium thiocyanate to 100 ml. of a solution which was 0.013 *F* in ferric nitrate and 0.6 *F* in nitric acid. The dissociation constant of the $Fe(SCN)^{++}$ complex has been recently determined by Frank and Oswalt (*3*) to have the value 7.25×10^{-3}, from which one calculates that the $Fe(SCN)^{++}$ concentration in the above solution was approximately 6.4×10^{-6} molal. Making use of this value and taking approximate values for the solubility products of silver chloride and silver thiocyanate to be 10^{-10} and 10^{-12}, respectively, one calculates that for no error in the titration the thiocyanate concentration should be 7.2×10^{-8} molal. From this value one calculates that if the ferric iron concentration were made 0.64 molal, a theoretically perfect titration would be possible under equilibrium conditions. If one is willing to tolerate an error of -0.1%, and the assumption is made that 2.5 millimoles of chloride are taken and that the final volume is 100 ml., one calculates that the thiocyanate should be 2.3×10^{-7} molal and that therefore the ferric iron concentration can be 0.2 molal.

As a result of these considerations an experimental study of the effect of increasing the ferric iron concentration has been made

Table I. Effect of Ferric Concentration on Potassium Thiocyanate Required for Detection of End Point

Expt. No.	$Fe(NO_3)_3$ Formality	KSCN Formality	SCN^- Calculated Molality
		No precipitate present	
1	0.5	1.1×10^{-5}	1.6×10^{-7}
2	0.3	5.2×10^{-6}	1.3×10^{-7}
3	0.2	1.8×10^{-6}	6.7×10^{-8}
4	0.1	3.5×10^{-6}	2.5×10^{-7}
		AgCl precipitate present	
5	0.2	3.5×10^{-6}	1.3×10^{-7}
6	0.1	4.1×10^{-6}	3.4×10^{-7}

and the results of this study together with two alternative procedures are presented below.

REAGENTS AND APPARATUS

Reagent grade chemicals were used in all cases. Volume measurements were used exclusively, the apparatus was especially calibrated, and appropriate temperature corrections were made. The silver nitrate and sodium chloride solutions were prepared from the appropriate weight of dried crystals, and by dilution to volume. The potassium thiocyanate solution was standardized against the silver nitrate solution. The ferric nitrate solution was prepared from the approximate weight of the reagent product and the concentration was determined iodometrically. These solutions, as well as the nitric acid, were tested for chloride.

DETERMINATION OF OPTIMUM ACID AND FERRIC CONCENTRATIONS

Preliminary experiments indicated that in solutions approximately 0.5 *F* in ferric nitrate the nitric acid had to be approximately 0.7 *F* in order to remove the color caused by partial hydrolysis of the iron. Accordingly, in order to provide a reasonable factor of safety, all experiments were carried out in solutions approximately 1 *F* in nitric acid. In the course of these experiments it was noted that, even in 1 *F* nitric acid, solutions which were more concentrated than 0.1 *F* in ferric nitrate had a slight residual color, grayish tinged with purple, which was not diminished by increasing the acid concentration. This color, probably that attributed by Rabinowitch and Stockmayer (*5*) to hydrated ferric ion, is perceptible with 0.15 *F*, and distinct with 0.3 *F*, ferric nitrate solutions, and made it desirable to determine at what ferric iron concentration the detection of the thiocyanate color was most sensitive.

The results of experiments for this purpose are tabulated in Table I. In the second column are shown the total—that is, the volume formal—concentrations of the ferric nitrate. The third column shows the formal concentrations of the thiocyanate calculated from the volume of the solution and the volume of 0.00214 *F* potassium thiocyanate added to produce a perceptible color. The fourth column shows the calculated volume molal concentrations of the thiocyanate ion; these values are approximate only, for no effort has been made to evaluate the activities of the various species. In experiments 5 and 6 a silver chloride precipitate of average size was present, together with a small excess of chloride, added to prevent metathesis of the precipitate to silver thiocyanate.

Titrations of chloride were then made with various concentrations of ferric nitrate, and as a result of the data obtained, which are shown in Table II, an indicator concentration of 0.2 *F* was adopted for future experiments. Experiments showed that somewhat better values were obtained by back-titrating with the silver solution to the disappearance of the color than by using the appearance of the color; scarcely more time is required, as the solution has to be vigorously shaken until the color remains permanent in the latter case. Solutions which were titrated to the appearance of the color showed no evidence of fading, even when allowed to stand, with frequent shaking, for periods up to 30 minutes. Experiments made at temperatures as low as 5° C. did not show an appreciable increase in the sensitivity of detection of the end point. In titrations in which an equivalent concentration of ferric sulfate was substituted for the nitrate the solution had a distinct greenish-yellow color which made the end point less distinct, and negative errors of about 0.5% were obtained.

Table II. Effect of Ferric Concentration on Accuracy of Titration of Chloride

Expt. No.	$Fe(NO_3)_3$ Formality	Wt. of Chloride, Mg.		Error	
		Taken	Found	Mg.	%
1a	0.30	104.7	105.1	+0.4	+0.38
b			104.8	+0.1	+0.10
2a	0.25	126.3	126.4	+0.1	+0.08
b			126.5	+0.2	+0.16
3a	0.20	104.7	104.6	−0.1	−0.10
b	0.20	104.7	104.7	0.0	0.00
4	0.15	63.26	63.12	−0.14	−0.22
5a	0.10	98.70	98.40	−0.30	−0.30
b			98.30	−0.40	−0.40
6a	0.05	98.68	98.01	−0.67	−0.68
b	0.05		97.80	−0.88	−0.90

The following procedure was then used to make a series of analyses of chloride solutions.

To 50 ml. of the chloride solution there was added a standard solution of silver nitrate, approximately 0.1 *N*, until, after vigorous shaking, a "clear point" was observed, then 2 to 3 ml. in excess were added. Then 17 ml. of 6 *F* nitric acid were added, followed by 10 ml. of 2.2 *F* ferric nitrate. The solution was titrated with an approximately 0.1 *F* standard solution of potassium thiocyanate to an easily perceptible pink color which was stable after 1 minute of vigorous swirling. The mixture was then back-titrated with the silver nitrate to the disappearance of the pink color. Comparison was made with a previously titrated solution containing a slight excess of silver nitrate or a prepared mixture of the same composition with a slight excess of silver nitrate. The final volume was between 105 and 110 ml. The room temperature varied from 24° to 27° C.

Ten analyses were made in which the quantity of chloride taken was varied from 40 to 200 mg.; the volume of approximately 0.1 *F* silver nitrate used ranged from 12 to 45 ml. and that of the thiocyanate from 0.5 to 5 ml. Stable end points were obtained, the average error was, without regard to sign, 0.06 mg. of chloride, and the maximum error was 0.11 mg. of chloride. Results of confirmatory analyses of solid samples made by essentially this procedure are shown in Table III.

ALTERNATIVE PROCEDURE

The obvious disadvantage of having to make two back-titrations, and of having to shake a full minute in order to attain stable conditions in the back-titration with thiocyanate, led to an investigation to ascertain if a small amount of thiocyanate could be added to the acid chloride solution containing the ferric nitrate, and the solution then titrated with the silver nitrate to the disappearance of the color.

A series of five preliminary experiments was made in which to the chloride in about 50 ml. of water there were added 17 ml. of 6 *F* nitric acid and 10 ml. of 2 *F* ferric nitrate, followed by either 0.04 ml. of 0.1072 *F* or 1.00 ml. of 0.01072 *F* potassium thiocyanate. The solutions were then titrated with silver nitrate to the disappearance of the indicator color. The solutions were shaken vigorously. Comparison solutions were used as in the procedure given above; the final volume was approximately 100 ml. Again stable end points were obtained, the average error without regard to sign was 0.08 mg. of chloride, and the maximum error was 0.22 mg. of chloride.

The possibility of error arising from decomposition of the thiocyanate during the titration was investigated by preparing solutions for the titration and then letting them stand for various times. There was no detectable diminution in the intensity of

Table III. Confirmatory Analyses

Expt. No.	Wt. of Sample, Mg.	$AgNO_3$, Ml.	KSCN, Ml.	% Cl Found
1. Analysis of Solid Unknown, 36.26% Cl				
		Procedure A		
		(0.1260 *F*)	(0.01072 *F*)	
1	453.6	36.93	1.00	36.24
2	361.7	29.47	1.00	36.27
3	361.7	29.48	1.00	36.27
		Procedure B		
			(0.1072 *F*)	
4	453.6	37.69	0.93	36.30
5	453.6	37.71	0.98	36.29
6	361.7	30.47	1.25	36.27
7	361.7	30.47	1.26	36.27

2. Analyses of Solutions

Procedure A. 25.00 ml. of NaCl solution taken, 1.00 ml. of 0.01031 *F* KSCN added

	$AgNO_3$		NaCl Formality	
	Ml. used	Formality	Found	Calculated
1	25.34	0.1035	0.1045	0.1047
2	24.84	0.1035	0.1028	0.1028
3	25.43	0.1035	0.1053	0.1051
4	25.65	0.1035	0.1062	0.1060
5	23.91	0.1107	0.1059	0.1058
6	25.33	0.1035	0.1048	0.1047
7	23.15	0.1107	0.1025	0.1026
8	22.15	0.1107	0.0981	0.0981
9	23.58	0.1107	0.1044	0.1044
10	23.55	0.1107	0.1043	0.1043

the color during these periods, which extended for as long as 2 hours, and the data from the titrations show no detectable effect of standing.

This alternative procedure is much more rapid than the first one, because it is possible to add the thiocyanate by means of a 1-ml. pipet. Less shaking is required to obtain a permanent end point, probably because adsorption of thiocyanate on the silver thiocyanate precipitate is minimized by the low thiocyanate ion concentration prevailing in the presence of the excess ferric ion. Should the end point be overrun, an additional portion of thiocyanate can be added and titrated; where rapid titrations are desired this procedure can be used to advantage.

In view of the above results the two following procedures are recommended:

Procedure A. That quantity of the substance to be determined which will require between 20 and 40 ml. of 0.1 *F* silver nitrate should be contained in about 30 ml. of a solution which also contains approximately 100 millimoles of nitric acid. Add 10 ml. of 2 *F* ferric nitrate (chloride-free) and 1.00 ml. of standard 0.01 *F* potassium thiocyanate by means of a 1-ml. pipet. Titrate, while vigorously swirling the mixture, to the disappearance of the color of the ferric thiocyanate complex. Compare the solution with one which has been similarly titrated, but to which an excess of 1 to 2 drops of the silver nitrate has been added. The final volume should be approximately 100 ml.

Procedure B. That quantity of the substance to be determined which will require between 20 and 40 ml. of 0.1 *F* silver nitrate should be contained in about 30 ml. of solution. Add 17 ml. of 6 *F* nitric acid and titrate with 0.1 *F* silver nitrate to a clear point, then add 1 to 2 ml. in excess. (If this titration can be made in a neutral solution a better clear point will be obtained; the acid should then be added.) Add 10 ml. of 2 *F* ferric nitrate and titrate with 0.1 *F* potassium thiocyanate until a distinct pink color is obtained which is permanent after 1 minute of rapid swirling. Back-titrate with the 0.1 *F* silver nitrate until the color just disappears. Compare the solution with one which has been similarly titrated to an excess of 1 to 2 drops of silver nitrate. The final volume should be approximately 100 ml.

CONFIRMATORY ANALYSES

Analyses were made by the above procedures of a commercial analyzed sample of a "soluble chloride" and of solutions for student analysis prepared by weighing out appropriate weights of dry reagent grade sodium chloride and diluting to volume in a 2-liter calibrated volumetric flask. The solid sample was analyzed gravimetrically by precipitation of silver chloride; the average of six determinations gave a mean of 36.26% chloride. The data obtained are shown in Table III.

ACKNOWLEDGMENT

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Radiometric Determination of Gold and Rhenium

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Methods have been developed for the determination of gold and rhenium using slow neutron activation analysis. On samples of iron meteorites weighing approximately 0.5 gram, concentrations of gold and rhenium in the range of a few parts per million are determined with a precision of 15% or better.

CONTINUING work on the development of analytical procedures utilizing the neutron pile, the pile irradiation method, as previously described (*2*), has been extended to gold and rhenium. The procedures have been applied specifically to iron meteorites. Weighed amounts of meteorite and the element whose concentration is sought are simultaneously irradiated in the thimble of the Argonne heavy water pile. A known amount of inert carrier of the element desired is added to a solution of the radioactive meteorite and to an aliquot of the irradiated standard. The activated atoms of the element along with the carrier are chemically separated from the meteorite. The ratio of the amount of carrier recovered to the amount added gives the chemical yield of the separation. A comparison of the decay curves of the meteorite and standard samples gives the concentration of the element in the meteorite. Absorption curves along with decay curves of both samples are compared and used as the criterion of completeness of separation.

SAMPLE PREPARATION

The specimens of meteorites subjected to analyses were of two forms, metal and metal powder. The metal powders resulted from the sawing of larger fragments and were irradiated without further treatment. Certain specimens were available only in the powder form. However, no marked difference in concentrations of these trace elements could be detected in the analyses of powder and solid metal taken from the same meteorite.

The solid samples were sawed into 0.3- to 0.5-gram samples with a Star 1032 high speed molybdenum hacksaw blade. These fragments were then filed to a smooth pellet. Samples that contained any discernible inclusions of troilite or schreibersite were rejected. The filed samples were then placed in 6 *N* hydrochloric acid for periods of 10 minutes to dissolve away the surface, washed with distilled water, and finally rinsed in alcohol.

COUNTING TECHNIQUES

Because both of the elements investigated give rise to beta-emitters with beta-energies greater than 0.5 m.e.v. upon slow neutron irradiation, thin-walled Eck-Krebs Geiger-Müller tubes enclosed in a lead shield were used for detecting the radiation. These tubes have a window thickness of about 35 mg. per sq. cm. The samples used for radioactivity measurements resulted from chemical procedures and were in the form of precipitates which were filtered on 1-cm. filter circles and mounted on cardboard backings. The samples were covered with cellophane. The counting measurements were made over an interval of 4 to 5 half-lives to determine the decay curve for each sample. For absorption curves, aluminum absorbers were used. Ten thousand counts were taken for each measurement.

METHOD APPLIED TO GOLD

Gold has one stable isotope, Au^{197}. This isotope captures a neutron to form Au^{198} with a half-life of 2.7 days (*10*). The radiation characteristics of the radioactive product are described elsewhere (*10*). Previous activation analyses for gold have been reported by Tobias and Dunn (*11*).

Individual samples of iron meteorites, along with gold powder as a standard, were irradiated in soft-glass vials in the thimble of the Argonne heavy water pile for a period of 1 hour. The main separation of gold from the eighty-odd elements in meteorites depends upon the extraction of gold chloride from a 10% hydrochloric acid solution into ethyl acetate (*6*). The gold chloride was later reduced with hydroquinone. This procedure provided a further separation from the platinum metals (*1*).

Chemical Procedure for Gold in Iron Meteorites. Dissolve 0.3 to 0.5 gram of irradiated meteorite in 20 ml. of aqua regia, add 30 mg. of auric ion carrier in the form of an aliquot from a solution of auric chloride, and evaporate to near dryness. Take up the residue in 30 ml. of 10% hydrochloric acid solution and extract the gold chloride into 30 ml. of ethyl acetate. Wash the ethyl acetate layer twice with 20 ml. of 10% hydrochloric acid solution. Evaporate the ethyl acetate layer to dryness on a steam bath, and take up the residue in 15 ml. of water and 5 ml. of concentrated hydrochloric acid. Bring the solution to a boil and add 10 ml. of a 5% aqueous solution of hydroquinone. Continue boiling for 20 minutes or until the gold metal coagulates into lumps. Filter the gold metal on 1-cm. paper circles. Wash with two 25-ml. portions of hot water and one 25-ml. portion of ethyl alcohol. Dry for 15 minutes at 110° C. and determine the weight of the precipitated gold.

The samples are now ready to count. The chemical yield for the over-all process averaged 75%. The meteoritic gold gave the reported half-life and an absorption curve that as identical with that of the standard gold sample.

Treatment of Gold Standard. Ten to 15 mg. of irradiated gold metal powder were dissolved in 10 ml. of aqua regia and diluted to 1000 ml. A 0.5-ml. aliquot of this solution along with an aliquot of the gold carrier was reduced with hydroquinone in acid solution as noted in the gold procedure above. This gave essentially the same counting rate as the gold recovered from the meteorite.

Correction for Self-Shadowing in Gold Standard. The gold atoms in the meteorite sample and in the standard gold powder did not encounter an identical neutron flux during the irradiation, owing to the phenomenon of self-shadowing—that is, the flux that reached the inner part of the standard sample may be entirely different from that which the skin of the specimen encounters. This may be expressed analytically for a sample by the standard equation (*9*)

$$f = f^o e^{-N_a \sigma_a x} \tag{1}$$

where f^o is the flux at the skin of the sample, f is the flux at a point x cm. inside the sample, σ_a is the total absorption cross section for the element, and N_a is the density in atoms per cubic centimer of the element in question.

In the case of the iron meteorite samples we may write the above equation as

$$f = f^o e^{-\sum\limits_a N_a \sigma_a x} \tag{2}$$

Using the average values of abundances of elements in iron meteorites (*3*) and the absorption cross sections of the element (*11*), one finds $f/f^o = 0.995$ where $x = 0.3$ cm., the maximum side length of the usual sample. Hence one may consider the flux through small specimens of iron meteorites as constant.

Flux losses due to scattering are small, inasmuch as the mean free path of the neutrons is much larger than the distance traveled through the sample in all cases considered in this work. For the case of the iron samples, the mean free path of the neutrons determined by the scattering cross section of about four barns is about 3 cm. The distance of travel through a sample is about 0.3 cm. Hence, upon integrating Equation 2 over the path length and dividing by the path length, one finds the average flux throughout the body to be 95% of the initial flux. This assumes that all the scattered neutrons are removed from the meteorite, which is certainly not the case.

As noted above, the standard used in the gold analyses was the metal powder and it may be treated as a foil with a layer thickness of about 0.05 cm. for the 10 mg. of sample used. The atomic activation cross section for gold is 96×10^{-24} sq. cm. (*12*). Equation 1 gives (f/f^o) minimum equal to 0.78 for gold.

Dilution experiments were devised to study the effect of self-shadowing and to correct the observed activities of the standard monitors for self-shadowing. In order to obtain an approximate correction, weighed portions of iron and gold powders were intimately mixed to simulate the iron meteorites. All the powders were sifted through a 200-mesh screen before the dissolving procedure. The self-shadowing in the largest powder particles sieved through a 200-mesh screen would reduce the flux by a maximum of 1.5% from Equation 1. Dilutions of gold were made from 100,000 to 6 p.p.m. by weight. Two hundred-milligram samples of the powders along with 10-mg. samples of the gold powder were irradiated under conditions identical to those used in the analyses.

The specific activity of the gold as a function of its weight concentration is plotted in Figure 1. In order to correct the gold analyses in the range of 1 to 4 p.p.m. by weight, all experimental results were divided by 2.34/1.63 = 1.44. The accuracy of this correction factor is limited by the self-shadowing of the particles used in the dilution experiment which was shown earlier to be 1.5%, the dilution error, and the error in the procedure itself. In the two samples run for each concentration, the specific activities were reproducible to 10%. For the above reasons the final gold results are given to two significant figures. Considerable improvement in the technique would result from the utilization of gold foil as the standard. This would appreciably reduce the self-shadowing correction.

RESULTS OF THE GOLD ANALYSES

Gold was analyzed in 45 iron meteorites and these results will be published in the near future. The standard deviation and the precision of the results on four meteorites are shown in Table I in order to demonstrate the internal consistency of the analyses on a given meteorite. The values are uncorrected for the self-shadowing of the standard. Spectroscopic iron and commercial aluminum were analyzed for gold following the above

Table I. Statistical Data of Analyses of Four Meteorites for Gold

(Uncorrected for self-shadowing of standard)

Canyon Diablo		Henbury		Xiquipilco		Odessa	
Run No.	Au, p.p.m., X_i	Run No.	Au, p.p.m., X_i	Run No.	Au, p.p.m., X_i	Run No.	Au, p.p.m., X_i
37	3.03	6	0.701	2	2.25	57	3.66
38	3.13	7	0.700	3	2.63	58	2.82
39	3.00	8	0.665	4	2.34	59	3.14
47	2.88	10	0.692	13	2.64	60	3.24
48	3.22	12	0.757	14	2.31	83	2.63
49	2.90	32	0.774	24	2.80	90	2.91
77	2.84	33	0.809	44	3.10	91	2.74
78	2.66	52	0.954	75	2.76	92	2.72
130	3.02	53	0.910	63	2.57	113	2.31
131	3.19	54	0.936	64	2.44	114	2.24
				81	2.74		
				82	2.60		
Arithmetic mean = x =	2.99		0.790		2.60		2.84
$\sigma = \sqrt{\frac{(x_1 - x)^2}{(n - 1)}}$	0.17		0.108		0.24		0.44
$\frac{\sigma}{x}$	5.7%		13.7%		9.23%		15.5%
Precision = $\frac{\sigma}{\sqrt{n}}$	0.05		0.034		0.07		0.14

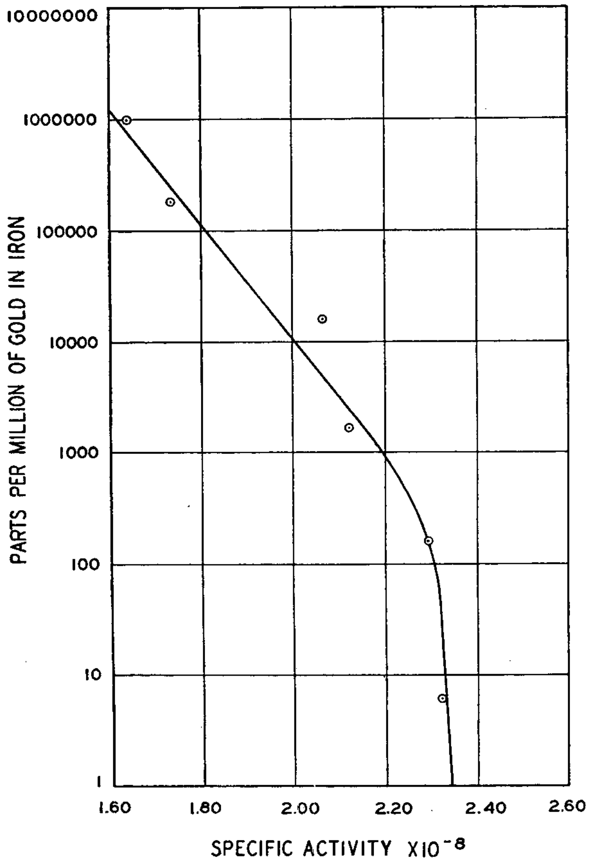

Figure 1. Specific Activity of Gold in Iron as a Function of Gold Concentration

procedure as blank runs. Upper limits were placed on these samples of 0.002 and 0.004 p.p.m. of gold, respectively.

In Table II are the results on two meteorites investigated in common by the Noddacks (*8*), Goldschmidt and Peters (*5*), and the authors.

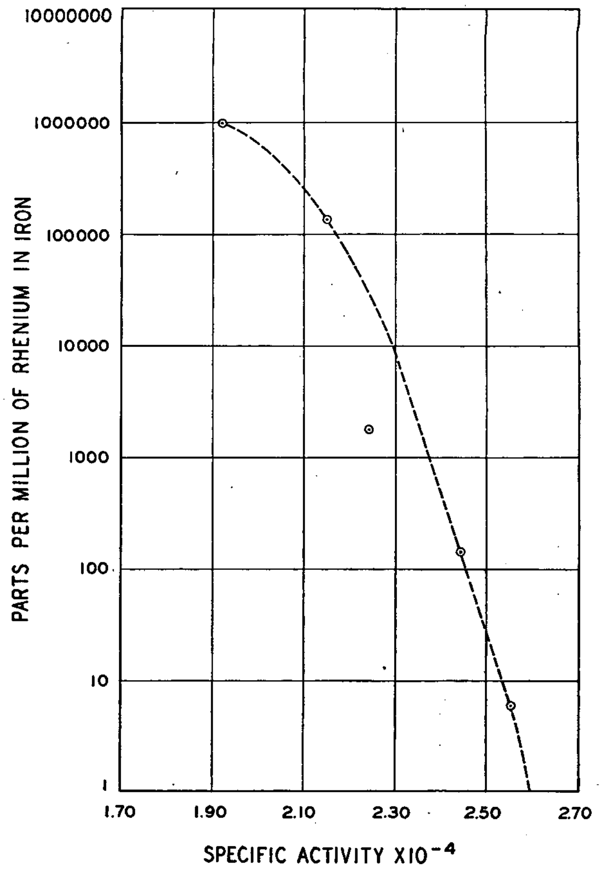

Figure 2. Specific Activity of Rhenium in Iron as a Function of Rhenium Concentration

Table II. Gold Contents of Canyon Diablo and Xiquipilco

Investigator	Canyon Diablo Meteorite, P.P.M.	Xiquipilco Meteorite, P.P.M.
Noddacks	1	0
Goldschmidt and Peters	5	10
Present investigation	2.1	1.8

METHOD APPLIED TO RHENIUM

Rhenium yields two prominent activities upon thermal neutron capture, Re^{186} with a half-life of 92.8 hours produced from Re^{185}, and Re^{188} with a half-life of 18.9 hours produced from Re^{187} (*10*). The two isotopes giving rise to the activities possess abundances of 37.07 and 62.93%, respectively (*10*). The radiation characteristics of these two activities are described elsewhere (*10*). The 92.8-hour half-life was used for decay and absorption measurements.

Individual samples of the meteorite along with 10 mg. of pure rhenium powder were irradiated in soft-glass vials. Thimble irradiations of 4 to 6 hours in the pile were necessary for adequate counting rates. The sample was allowed to cool for 2 or 3 days after the end of the bombardment before working the samples. The procedure for separating rhenium in meteorites is based upon the method of separating technecium from fission products (*4*). The main isolation, from molybdenum is accomplished by the distillation of rhenium heptoxide from a sulfuric acid solution of the meteorite. Separation from arsenic, selenium, germanium, and other constituents with volatile halides is accomplished by repeated evaporations to dryness of a hydrobromic acid solution of the meteorite.

Chemical Procedure for Rhenium in Iron Meteorites. Dissolve 0.3 to 0.5 gram of irradiated meteorite in 20 ml. of concentrated hydrobromic acid, add 10 to 15 mg. of rhenium in the form of standardized potassium perrhenate carrier, and evaporate to dryness. Add 10 ml. more of hydrobromic acid and repeat evaporation, take up the residue in 10 ml. of water, add 10 ml. of concentrated sulfuric acid, and distill in a current of air until 2 or 3 ml. of sulfuric acid remain in the flask. Collect the distillate in 20 ml. of water in a 50-ml. centrifuge tube kept in an ice bath. Place the centrifuge tube in a steam bath and pass in hydrogen sulfide until the coagulation of rhenium heptasulfide is complete. Centrifuge and discard the supernate. Wash the rhenium heptasulfide with 10 ml. of water. Dissolve the rhenium heptasulfide in 1 ml. of nitric acid, add 5 ml. of concentrated hydrobromic acid, and evaporate to dryness. Take up residue in 20 ml. of water. Add 5 mg. of ferric iron in the form of the ferric chloride. Add ammonium hydroxide drop by drop till precipitation of ferric hydroxide occurs. Heat on steam bath, centrifuge, and discard the precipitate. Repeat ferric hydroxide scavenging. Add 5 ml. of a 1% aqueous solution of tetraphenyl-arsonium chloride. Let the precipitate of tetraphenyl arsonium perrhenate stand for 20 minutes. Filter, wash with two 25-ml. portions of hot water and 25 ml. of alcohol. Weigh, dry 15 mintues at 110° C., and mount for counting.

Table III. Rhenium Analyses

Henbury Meteorite		Xiquipilco Meteorite	
Run No.	Re, p.p.m.	Run No.	Re, p.p.m.
5	1.3	14	0.30
6	1.6	17	0.26
9	1.3	19	0.25
13	1.6	22	0.30

Treatment of Rhenium Standard. Ten to 15 mg. of irradiated rhenium metal were dissolved in 10 ml. of nitric acid and diluted to 1000 ml. A 1-ml. aliquot of this solution was added to the carrier aliquot. The combined solution was diluted to 50 ml. The standard was then treated with the tetraphenyl arsonium chloride as described above.

As in the case of gold, the rhenium standard was subject to self-absorption due to its high absorption cross section of 84×10^{-24} sq. cm. (*10*).

Similar dilution experiments were carried out to correct for the self-shadowing in the standard. The specific activity of the rhenium as a function of its weight concentration is plotted in Figure 2. The errors in the procedure are similar to those noted under the gold dilution experiment. To compensate for the high results due to the self-shadowing of the standard, the experimental values have been divided by a factor of $2.6/1.92 = 1.35$. The results are given to two significant figures, as, again, the results were reproducible to only 10% of the total specific activity for the two samples of each concentration range analyzed. That the plot of the specific activity of the Re^{188} activity against concentration was identical with Figure 2 indicated that the self-shadowing is mainly due to the thermal neutron absorption and not to the resonance cross section observed in Re^{185}.

RESULTS OF RHENIUM ANALYSIS

Analyses of rhenium were made in five iron meteorites and these results will be published elsewhere. Preliminary results on two meteorites corrected for self-absorption are listed in Table III.

The Noddacks report an average value of 6.2×10^{-3} p.p.m. of rhenium in iron meteorites as a result of spectroscopic analysis (*7*).

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Determination of Bromine and Chlorine in Gasoline

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ALTHOUGH there are several methods for the determination of halogen in organic compounds, heretofore there has been no satisfactory procedure for the analysis of dilute solutions of halogen compounds in organic solvents, especially if the halide is relatively volatile or difficult to decompose. A specific example of the problem is the determination of ethylene halides present in gasolines, where the total amount of halogen is less than 0.01 equivalent per liter.

The use of sodium for the decomposition of organic halides is well known. However, sodium in alcohol (*7*) or alcoholic potassium hydroxide gives low results, because the ethylene halides present in gasoline first react to give the highly volatile vinyl halides; these are stable and escape from the reaction system. Better recoveries are obtained by the use of sodium in liquid ammonia (*4*), but this method is not especially suitable for routine use. Methods based on complete oxidation of the sample, either dry (*1, 5*) or wet (*8*), restrict the size of the sample so that microprocedures are necessary in the final stages of the analysis. In the lamp method (*10*) larger samples may be taken but the use of the standard A.S.T.M. lamp (*2*) in this procedure gives results as much as 25% low for bromine and 5% low for chlorine, especially if tetraethyllead is present. The use of a modified burner in a recently reported procedure shows good recovery for both halides (*9*).

A highly reactive organosodium compound prepared from halogen-free reagents would appear to be the ideal reagent for the decomposition of organic halides. Although the preparation of such compounds is generally difficult, Scott, Walker, and Hansley (*6*) have shown that the addition compounds of sodium and some aromatic hydrocarbons can be conveniently prepared in certain activating solvents like dimethyl ether and ethylene glycol dimethyl ether. The use of disodium naphthalene, prepared in this manner, for the determination of carbon-bonded halogen has been discussed in a recent analytical note (*3*).

Preliminary experiments showed that organosodium reagents

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Table I. Effect of Reaction Time on Halogen Analysis

Halide Present	Reaction Time, Min.	Halogen, G./Gal.		% Error
		Added	Found	
Ethylene bromide	10	3.61	3.59	−0.5
			3.63	+0.5
			3.59	−0.5
	30	3.61	3.55	−1.7
			3.54	−1.9
			3.47	−1.9
	210	3.38	3.27	−3.3
			3.31	−2.1
			3.28	−3.0
			3.32	−1.8
	465	3.42	3.29	−2.7
			3.30	−2.4
			3.34	−1.2
			3.26	−3.5
	Overnight	3.15	3.07	−2.6
Ethylene chloride	10	1.24	1.23	−0.8
			1.23	−0.8
			1.23	−0.8
	30	1.24	1.22	−1.6
			1.22	−1.6
	120	1.24	1.22	−1.6
			1.22	−1.6
			1.22	−1.6
	Overnight	1.24	1.24	0.0
			1.23	−0.8
			1.24	0.0

gave good recoveries of halogen in gasoline, even in the presence of tetraethyllead, and on this basis the method described below was developed.

DEVELOPMENT OF DISODIUM BIPHENYL PROCEDURE

After exploratory experiments on several compounds including disodium naphthalene, disodium anthracene, and the ketyl from benzophenone, efforts were concentrated on disodium biphenyl. This reagent is reactive at room temperature, giving recoveries of halogen close to 100%, and the aqueous extract of gasoline treated with the biphenyl compound contains a minimum of organic material—a matter of some importance, as shown below.

The following basic procedure was used in elaborating the present analytical method:

> To a sample of gasoline, diluted with benzene, was added an excess of 0.5 *N* solution of disodium biphenyl in ethylene glycol dimethyl ether. After approximately 30 minutes, the excess reagent was decomposed with water, the alkali formed was neutralized, and the organic phase was extracted six times with water. The extract was made alkaline, heated to boiling, and treated with hydrogen peroxide to remove organic matter, then was cooled, acidified, and filtered. Potentiometric titration was usually employed to determine the halide. Tetraethyllead was shown to have no effect on the analysis. The subsequent development is described in the following sections.

Effect of Reaction Time. Tests were made on known blends of ethylene halides in an aviation gasoline by varying the reaction time, as shown in Table I. These data not only show that a short reaction period gives accurate determination of both bromine and chlorine, but indicate that bromine determinations are less accurate when longer reaction times are used.

Although a 10-minute reaction period is sufficient, the time of reaction was standardized at 15 to 30 minutes, because the additional time is required by the analyst to prepare the equipment necessary for the subsequent steps.

Number of Extractions with Water Required. Using a blend of ethylene bromide in the same aviation fuel, tests were made to determine the number of extractions with water required to remove all of the inorganic halogen. As shown in Table II, two 10-ml. extractions appear to be ample.

Effect of Normality of Reagent. The activity of the disodium biphenyl reagent was determined by titration with a solution of alcohol in benzene, assuming that the typical blue-green color of the reagent is an indication of active sodium. Thus, to determine the active sodium content, a 20-ml. sample was titrated with a 1.0 *N* solution of alcohol in benzene to the disappearance of color.

Because the halogen recovery depends on the active sodium content of the reagent, tests were made to determine the effect of low active sodium content on the analysis. The results, given in Table III, indicate that a reagent as dilute as 0.25 *N* is satisfactory (in practice, a reagent less than 0.5 *N* is not recommended).

Effect of Different Oxidants. In the first tests of the new reagent employing gravimetric procedures, it was observed that a small amount of organic matter removed from the gasoline was precipitated along with the silver halide. Most of this organic matter could be destroyed by adding hydrogen peroxide and evaporating to approximately 25 ml. Because it was observed that additional treatments with hydrogen peroxide improved the analysis, other oxidizing agents were tested.

Table II. Effect of Number of Extractions with Water

No. of Extractions	Bromine, G./Gal.		% Error
	Added	Found	
2	3.61	3.58	−0.8
		3.57	−1.1
		3.60	−0.3
3	3.61	3.62	+0.3
		3.57	−1.1
		3.58	−0.8
6	3.61	3.54	−1.9
		3.58	−0.8
		3.56	−1.4

Some of the organic material in the extract can be volatilized and some can be removed by filtration. The problem of oxidation therefore was simplified by evaporating the extract to low volume, acidifying, and filtering the solution prior to oxidation. This procedure was followed in testing sodium peroxide and ammonium persulfate.

Table III. Effect of Normality of Reagent on Halogen Analysis

Normality of Reagent, Active Sodium	Bromine, G./Gal.			Chlorine, G./Gal.		
	Added	Found	% Error	Added	Found	% Error
0.25	3.23	3.26	+1.0	1.24	1.24	0.0
		3.27	+1.3		1.24	0.0
		3.29	+1.7			
0.50	3.23	3.26	+1.0	1.24	1.23	−1.0
		3.23	0.0		1.22	−1.5
		3.29	+1.7		1.22	−1.5
0.80	3.23	3.22	−0.3	1.24	1.22	−1.4
		3.22	−0.3		1.23	−0.8
		3.22	−0.3		1.23	−0.8

One-hundred milliliter portions of several halogen-free gasolines known to give difficulty in analysis were treated with 25 ml. of disodium biphenyl reagent in ethylene glycol dimethyl ether. After decomposing the excess reagent and extracting with water, 25.00-ml. aliquots of 0.01616 *N* sodium bromide solution and of 0.03231 *N* sodium chloride solution were added to the extracts. The resulting solutions duplicated the amounts of bromine and chlorine present in a 100.00-ml. sample of gasoline containing 3.00 ml. of tetraethyllead per gallon as motor mix antiknock fluid (1.222 grams of bromine and 1.084 grams of chlorine per gallon). The halides in the extracts were determined after (1) evaporating to low volume, acidifying, filtering, and titrating without oxidation; (2) oxidizing the extract by adding 2 ml. of 30% hydrogen peroxide and evaporating to approximately 25 ml.; (3) evaporating to low volume, acidifying, filtering, and oxidizing with sodium peroxide; and (4) same as (3) but using ammonium persulfate in place of sodium peroxide. When sodium peroxide or ammonium persulfate was used, 10 ml. of 10% sodium arsenite solution were added to the extract after oxidation to reduce any bromate that might have formed. The halides in the extracts were determined by potentiometric titration with 0.1 *N* silver nitrate solution. The results, given in Table IV, indicate that oxidation with ammonium persulfate gives the most accurate analyses.

A method, accurate to within ±2%, was developed for the determination of bromine and chlorine in gasoline. Disodium biphenyl was found to be an effective reagent for decomposing the ethylene halides. The reagent can be prepared satisfactorily in ethylene glycol dimethyl ether and in tetraethylene glycol dimethyl ether; other ethers were tested, but were found unsatisfactory. A sample of the gasoline to be analyzed is diluted with benzene and treated with an excess of 0.5 *N* solution of disodium biphenyl. After approximately 30 minutes, the excess reagent is decomposed with water, the alkali formed is neutralized, and the sodium halides are extracted from the organic phase with water. The halides are determined by potentiometric titration using a silver–silver chloride electrode system. Tetraethyllead does not interfere. The method is also applicable to the determination of carbon-bonded bromine and chlorine in organic compounds other than ethylene halides.

Solvents for Disodium Biphenyl Reagent. Most of the experimentation during the development program was carried out with solutions of disodium biphenyl prepared in ethylene glycol dimethyl ether. In addition to this ether, tetraethylene glycol dimethyl ether was shown to be a satisfactory solvent. The reagent prepared in this ether was found to be slightly more stable. On the other hand, ethylene glycol diethyl ether (diethyl Cellosolve) is less suitable. Slow decomposition of the reagent occurs in this ether and low results are obtained.

Sodium peroxide is an acceptable oxidizing agent with either methyl ether solution of disodium biphenyl, but oxidation with ammonium persulfate gave low, erratic results when used with the reagent prepared in tetraethylene glycol dimethyl ether.

REAGENTS

Ethylene Glycol Dimethyl Ether, Commercial Grade. Distill the ether and collect the fraction boiling from 82° to 85° C. Place 2 liters of the distilled material in a stoppered 3-liter, three-necked, round-bottomed flask equipped with a source of dry nitrogen and a stirrer. Add 35 grams of recrystallized biphenyl while flushing the flask with nitrogen. Then, maintaining a slow, steady stream of nitrogen, add 5.5 grams of metallic sodium in the form of coarse chips, and stir the mixture. The green disodium biphenyl will begin to form immediately if the ether is free of impurities. If moisture and other impurities which react with sodium are present, reflux the ether over sodium for several hours prior to the distillation; otherwise, the impurities will react with the sodium preferentially. Distill the ether from the solution, using a short fractionating column. Collect the fraction distilling between 83° and 84° C. Store the ether in a glass-stoppered, brown bottle containing clean copper gauze to prevent the formation of peroxide.

Tetraethylene Glycol Dimethyl Ether, Commercial Grade. Place 200 ml. of tetraethylene glycol dimethyl ether in the apparatus described above. Add 75 grams of recrystallized biphenyl and, while the mixture is being stirred, add 10 grams of freshly cut sodium chips. Heat the mixture to 75° to 80° C. When the sodium has reacted, add 1800 ml. of tetraethylene glycol dimethyl ether, stir the mixture for a few minutes, and distill the ether from the mixture at approximately 10-mm. pressure.

Biphenyl, commercial grade.

Sodium, analytical reagent grade.

Benzene, analytical reagent grade.

Nitric Acid, Dilute. Add one part of concentrated nitric acid (specific gravity 1.42) to one part of distilled water.

Ammonium Persulfate, Analytical Reagent grade. Store in a cool, dark place.

Sodium hydroxide, analytical reagent grade pellets.

Sodium Arsenite, 10%. Dissolve 60 grams of sodium hydroxide in distilled water and add 60 grams of arsenic trioxide. Stir the mixture until the arsenic trioxide dissolves, and dilute to 1 liter with distilled water.

Sodium peroxide, analytical reagent grade.

Methyl orange indicator solution (0.1 gram per 100 ml. of water).

Disodium Biphenyl Prepared in Ethylene Glycol Dimethyl Ether. Place 200 ml. of purified ethylene glycol dimethyl ether and 77 grams of biphenyl in a 1-liter, three-necked, round-bottomed flask fitted with a nitrogen inlet tube, a sealed stirrer, and a loose-fitting cork. Flush the flask with nitrogen, and while continuing the flow of nitrogen, start the stirrer and add 12 grams of sodium in the form of coarse chips. In ether prepared as above, the reaction will begin at once with the formation of color, and is usually complete in about 2 hours, when all the lumps of sodium have disappeared. Determine the sodium content by decomposing a sample of the material in water and titrating the alkali with standard acid using methyl orange as the indicator.

The reagent oxidizes readily in air. Acidimetric titration of a sample that has been oxidized will give not the active sodium content, but the total sodium content. The active sodium content may be determined by titration with an alcohol-benzene solution as follows:

Prepare a 1.0 *N* alcohol solution by diluting 46 grams of absolute alcohol to 1000 ml. with benzene. Titrate a measured portion of the reagent, preferably 20 ml., with the alcohol-benzene solution, and calculate the active sodium content as follows:

$$N \text{ reagent} = \frac{\text{ml. of ethyl alcohol}}{\text{ml. of reagent}}$$

Table IV. Effect of Method of Oxidation on Halogen Analysis

(Amount of halogen added: 1.222 grams of Br per gal., 1.084 grams of Cl per gal.)

Fuel No.	Oxidizing Agent		Bromine Found		Chlorine Found	
	Compound	Amount, g.	G./gal.	% error	G./gal.	% error
1			1.433	+17.3	1.066	−1.7
			1.540	+25.0	1.071	−1.2
			1.488	+21.8	1.062	−2.3
	Hydrogen peroxide	2 ml.	1.269	+3.8	1.162	+7.2
			1.259	+3.0	1.154	+6.5
	Sodium peroxide		1.244	+1.8	1.074	−0.9
			1.244	+1.8	1.082	−0.2
			1.241	+1.6	1.082	−0.2
	Ammonium persulfate	2	1.208	−1.2	1.092	+0.7
			1.214	−0.7	1.078	−0.6
			1.211	−0.9	1.089	+0.5
2	Sodium peroxide	5	1.211	−0.9	1.082	−0.2
			1.226	+0.3	1.080	−0.4
	Ammonium persulfate	2	1.232	+0.8	1.071	−1.2
			1.205	−1.4	1.092	+0.7
3	None		1.336	+9.3	1.042	−3.9
			1.281	+4.8	1.057	−2.5
	Sodium peroxide	5	1.250	+2.3	1.077	−0.7
			1.214	−0.7	1.082	−0.2
	Ammonium persulfate	2	1.226	+0.3	1.085	+0.1
			1.232	+0.8	1.082	−0.2
4	None		1.354	+10.8	1.086	+0.2
			1.357	+11.8	1.059	−2.3
	Sodium peroxide	5	1.238	+1.3	1.085	+0.1
			1.256	+2.8	1.063	−1.9
	Ammonium persulfate	2	1.250	+2.3	1.080	−0.4
			1.238	+1.3	1.090	+0.6
5	None		1.464	+19.8	1.093	+0.8
			1.449	+18.6	1.093	+0.8
	Hydrogen peroxide	2 ml.	1.314	+7.5	1.080	−0.3
			1.327	+8.6	1.058	−2.4
	Sodium peroxide	5	1.235	+1.1	1.081	−0.3
			1.232	+0.8	1.077	−0.7
	Ammonium persulfate	2	1.229	+0.6	1.077	−0.7
			1.214	+0.7	1.081	−0.3

If the color of the reagent changes markedly, or if there is some doubt as to the activity of the reagent, the active sodium content should be redetermined. If the reagent is less than 0.5 *N*, it should not be used. In the dark under nitrogen, the reagent is stable for about 2 weeks. The preparation described is sufficient for approximately ten determinations.

Disodium Biphenyl Prepared in Tetraethylene Glycol Dimethyl Ether. Place 100 ml. of purified tetraethylene glycol dimethyl ether and 77 grams of biphenyl in the apparatus described above, sweeping out air with nitrogen in the same way. Start the stirrer and add 9 grams of sodium in the form of coarse chips. When the sodium has been added, apply heat to the flask by means of an electric hot plate until the temperature reaches approximately 70° C. Remove the hot plate, continue the stirring for 1 hour, then add 100 ml. more of tetraethylene glycol dimethyl ether and cool to room temperature. Determine the total sodium content and the active sodium content as described above.

Table V. Comparison of Analysis Obtained Using Disodium Biphenyl in Different Solvents

	Tetraethylene Glycol Dimethyl Ether, Sodium Peroxide Oxidant						Ethylene Glycol Dimethyl Ether, Ammonium Persulfate Oxidant					
	Bromine, G./Gal.			Chlorine, G./Gal.			Bromine, G./Gal.			Chlorine, G./Gal.		
Fuel	Added	Found	% error	Added	Found	% error	Added	Found	% error	Added	Found	% error
No. 1 + motor mix fluid	1.133	1.119	−1.2	1.005	1.008	+0.3	1.166	1.152	−1.2	1.035	1.021	−1.4
		1.113	−1.8		1.004	−0.1		1.146	−1.7		1.021	−1.4
		1.113	−1.8		1.004	−0.1		1.149	−1.5		1.021	−1.4
No. 2 + motor mix fluid	1.116	1.151	+3.1	0.990	0.979	−1.1	1.252	1.275	+1.8	1.101	1.092	−0.8
		1.145	+2.6		0.990	0.0		1.272	+1.6		1.098	−0.3
		1.148	+2.9		0.987	−0.3		1.272	+1.8		1.091	−0.9
		1.107	−0.8		0.970	−2.0						
		1.113	−0.3		0.969	−2.1						
		1.087	−2.6		0.969	−2.1						
		1.090	−2.3		0.974	−1.6						
		1.079	−3.3		0.965	−2.5						
No. 5 + motor mix fluid	1.195	1.131	−5.4	1.061	1.004	−5.4	1.195	1.155	−3.3	1.061	1.018	−4.1
		1.183	−1.0		1.039	−2.1		1.183	−1.0		1.021	−3.8
		1.033	−13.6		0.966	−9.0						
		1.085	−9.2		0.973	−8.3						
		1.115	−6.7		1.013	−4.5						
		1.152	−3.6		1.048	−1.2						
		1.121	−6.2		1.036	−2.4						
		1.134	−5.1		1.027	−3.2						
		1.146	−3.3		1.052	−0.8						
		1.140	−3.8		1.033	−2.6						
		1.174	−1.8		1.036	−2.4						
No. 6 + aviation mix fluid	3.258	3.277	+0.6	None	None	None	2.319	2.345	+1.1	None	None	..
		3.262	+0.1					2.345	+1.1			
		3.262	+0.1					2.354	+1.5			
No. 7 + motor mix fluid	1.103	1.120	+1.5	0.979	0.967	−1.2	1.060	1.045	−1.4	0.872	0.869	−0.3
		1.120	+1.5		0.964	−1.5		1.042	−1.7		0.871	−0.1
		1.120	+1.5		0.965	−1.4		1.039	−2.0		0.875	+0.3

Table VI. Analyses of Halogen Compounds Other Than Ethylene Halides

	Halogen, Wt. %			
Compound	Calcd.	Found	% Error	Purity of Sample
CCl_4	92.19	91.74	−0.5	E.K., practical grade, redistilled
		91.54	−0.7	
C_2H_5Cl	54.96	55.11	+0.3	Commercial, high purity
		55.34	+0.7	
		55.21	+0.5	
C_2HCl_3	80.95	80.44	−0.6	Technical material, redistilled
		81.09	+0.2	
C_2Cl_4	85.53	85.88	+0.4	Dow technical, as received
sec-C_4H_9Cl	38.30	38.28	−0.1	E.K., redistilled
		38.34	+0.1	
C_6H_5Br	50.89	51.05	+0.3	E.K., as received
		51.09	+0.4	
p-$C_6H_4Cl_2$	48.26	48.34	+0.2	E.K., as received
		48.35	+0.2	
p-$C_6H_4Br_2$	67.77	67.84	+0.1	E.K., as received
		68.00	+0.3	
$(ClC_2H_4)_2O$	49.58	49.57	0.0	E.K., as received
		49.68	+0.2	
p-ClC_6H_4OH	27.58	27.54	−0.1	E.K., practical grade, redistilled and recrystallized
		27.53	−0.2	

PROCEDURE

Place 50 ml. of benzene in a 250-ml. Squibb-type, glass-stoppered separatory funnel and add 25 ml. of disodium biphenyl reagent. Pipet a 100-ml. aliquot of the gasoline to be analyzed into the mixture, stopper the funnel, shake vigorously for 20 to 30 seconds, and vent. The color of the hydrocarbon phase may vary from gray to deep green, depending on the solubility of the reagent in the gasoline and the quantity of halogen in the sample. A gray suspension after shaking indicates insufficient reagent; additional reagent should then be added in an amount sufficient to give a permanent green color.

Allow the mixture to stand 15 to 30 minutes, then add water to decompose the reagent; decomposition will be evidenced by the disappearance of the green color. Stopper and invert the funnel and vent the gas evolved. Shake the mixture to promote the decomposition and continue shaking until no more gas is evolved. Allow the gasoline and water layers to separate and drain the water layer into a 400-ml. beaker. Wash the sides of the funnel with 10 ml. of distilled water and, without shaking, drain the water layer into the beaker, rinsing the stem of the funnel. Add 10 ml. of distilled water and 1 ml. of dilute nitric acid, shake vigorously, and drain the water layer into the beaker. Repeat the extraction twice with distilled water. Evaporate the combined extracts to approximately 25 ml., cool, and acidify with dilute nitric acid using methyl orange as the indicator. Filter the solution through fine-textured filter paper with pulp, and collect the filtrate in a 600-ml. beaker.

If the disodium biphenyl was prepared in ethylene glycol dimethyl ether, add 2 grams of sodium hydroxide and 2 grams of ammonium persulfate to the filtrate. Because one of the decomposition products of ammonium persulfate is sulfuric acid, it is necessary to check the solution occasionally with methyl orange indicator solution to assure alkalinity during the evaporation. A light yellow indicator color is satisfactory indication of alkalinity. The 2 grams of sodium hydroxide should ordinarily be sufficient, but more should be added if the solution becomes acid. When the solid is dissolved, evaporate the solution to approximately 50 ml., and add 10 ml. of sodium arsenite solution. Continue the boiling for 10 minutes, then remove the sample from the hot plate. When cool, determine the halide by potentiometric titration with 0.1 *N* silver nitrate, using a silver–silver chloride electrode system.

If the disodium biphenyl was prepared in tetraethylene glycol dimethyl ether, add 5 grams of sodium peroxide, evaporate the solution to approximately 50 ml., then add 10 ml. of sodium arsenite solution. Continue the boiling for 10 minutes; when cool, determine the halide as above.

Blank. A blank determination should be made on all reagents and this blank subtracted from the total volume of silver nitrate used. For bromide determinations the blank can usually be disregarded if the halide is determined potentiometrically, inasmuch as bromide is titrated first and the blank is usually chloride or other ion that titrates at a potential reached after the bromide end point. The interfering substances extracted from many gasolines add slightly to the chloride titration even after oxidation with persulfate, and for greatest accuracy, a blank should be determined on the gasoline.

CALCULATION

Calculate the bromine and/or chlorine content of the gasoline as follows:

$$\text{Grams of Br/gal.} = \frac{302.50(A - C)B}{V}$$

$$\text{Grams of Cl/gal.} = \frac{134.22(D - E)B}{V}$$

where A = milliliters of silver nitrate required to titrate the bromide
B = normality of silver nitrate
C = milliliters of silver nitrate required to titrate the bromide in the blank
D = milliliters of silver nitrate required to titrate the chloride
E = milliliters of silver nitrate required to titrate the chloride in the blank
V = milliliters of sample used

RESULTS

Indications of the accuracy and precision of analyses obtainable by the disodium biphenyl method are given in Tables I to V. As shown in Tables IV and V, the preferred combination of disodium biphenyl, ethylene glycol dimethyl ether, and ammonium persulfate gives results within ±2% of the actual bromine and chlorine contents.

Applicability of Method Apart from Gasoline Analysis. To test the applicability of the method to the determination of organic halogen compounds other than ethylene halides, a few duplicate analyses were made on benzene solutions containing approximately 1% halo compound, with the good accuracy shown in Table VI.

ACKNOWLEDGMENT

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Determination of Fluorine (and Carbon) in Fluorinated Hydrocarbons

High Temperature Combustion Technique

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Fluorine in highly fluorinated organic compounds is ordinarily determined by tedious methods, whereas carbon, in the presence of fluorine, cannot easily be determined by the conventional combustion procedure. A method is described whereby the fluorinated material is burned 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; the carbon is simultaneously converted to carbon dioxide and is absorbed in Ascarite in the conventional manner. Partially or completely fluorinated compounds, in either solid or liquid state, may be analyzed by the method in about 1.5 hours. The accuracy is comparable to that obtained by more lengthy procedures.

BECAUSE of the exceptional activity of fluorine and hydrogen fluoride, the determination of fluorine frequently presents a problem not encountered in the case of the other halogens. In the analysis of organic compounds, the problem is further complicated by the necessity for first decomposing the material so as to convert the fluorine into the ionic form. Highly fluorinated compounds are especially difficult to decompose in this manner, because they contain a large number of the relatively stable carbon-fluorine bonds. With the increased interest in polyfluorinated materials of the type described in the Manhattan Project and recent literature (*2*), the development of a reasonably rapid and accurate analytical method has become extremely desirable.

Several methods have been employed for the determination of fluorine and other halogens in highly fluorinated compounds. Miller and his co-workers (*5*) modified the Vaughn and Nieuwland method (*8*), decomposing the material by sodium in liquid ammonia and precipitating the fluoride as lead chlorofluoride. Excellent results were reported, but the reagents used are objectionable to handle and the procedure is somewhat lengthy. Kimball and Tufts (*3*) designed a nickel bomb for the decomposition of fluorocarbons by the action of metallic potassium at an elevated temperature. This procedure is also lengthy, because the fluorine must be isolated by distillation as fluosilicic acid before final determination.

A combustion method for the simultaneous determination of carbon and fluorine was developed by Teston and McKenna (*7*). However, the procedure was not directly applicable in the presence of hydrogen, and the analysis of a single completely fluorinated compound yielded low fluorine results. Bockemüller (*1*) proposed a method involving combustion in a platinum tube which he applied to the analysis of compounds containing one or two atoms of fluorine in the molecule. More recently Schumb and Radimer (*6*) applied a combustion technique to the determination of fluorine in highly fluorinated volatile compounds. The method reported herein employs the same principle. However, whereas the Schumb and Radimer method is designed for gases and volatile liquids, the proposed procedure may be applied to any compound boiling higher than about 60° C. It has the furthur advantage that carbon may be determined simultaneously. Elements other than carbon, oxygen, hydrogen, and fluorine interfere, however, and require modification of the basic procedure.

The method is based on the principle that at high temperatures the combustion of fluorocarbons in a mixture of oxygen and water vapor results in a quantitative decomposition to yield carbon dioxide and hydrogen fluoride. The combustion is carried out in a tube made of platinum, which effectively resists the action of hydrogen fluoride. The hydrogen fluoride is absorbed in water, while the carbon dioxide largely passes through the aqueous solution and is absorbed in Ascarite. Any dissolved carbon dioxide is swept out and recovered prior to the final estimation of the fluorine, which is by simple alkalimetric titration of the hydrofluoric acid.

APPARATUS

The assembled apparatus is shown in Figure 1.

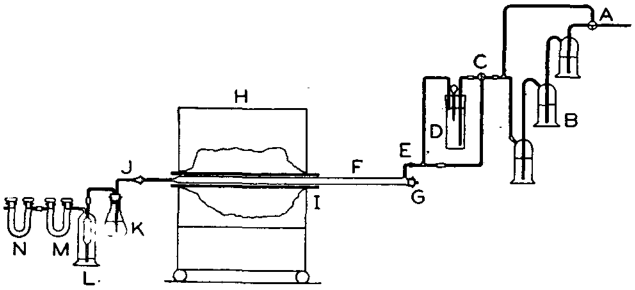

Figure 1. Combustion Train Assembly

The gas saturator, *B*, consists of a series of three gas-washing bottles containing water and through which the oxygen stream may be directed by means of the 3-way stopcock, *A*. The oxygen is first purified by passing through Ascarite.

The vaporizer, *D*, is used only when volatile samples are analyzed. It consists of a cylindrical flask of approximately 100-ml. capacity, fitted with a 3-hole neoprene stopper into one hole of which the vial containing the sample is inserted (Figure 2). By means of the 3-way stopcock, *C*, the vaporizer may be bypassed when nonvolatile materials are analyzed.

The combustion tube, *F*, is a platinum tube 100 cm. long, 1.25 cm. in inside diameter, and 0.4 to 0.5 mm. in wall thickness. The inlet end is fitted with a Ŧ 14/20 hollow platinum plug, *G*, and a side arm, *E*, to which a section of 6-mm. soft-glass tubing is fused. The outlet fits into a 5-mm. inside diameter platinum delivery tube, *J*, by means of a Ŧ 7/25 joint. The combustion tube contains a 10-cm. (4-inch) roll of 50-mesh platinum gauze and is supported in the furnace by a $^7/_8$-inch McDanel high-temperature combustion tube, *I*. The platinum tube used by Miller *et al.* for the determination of hydrogen in hydrohalocarbons (*4*) should be suitable.

The furnace, *H*, is a Burrell Model A-13 furnace, fitted with wheels and mounted on a track so that it may be easily moved. This permits different sections of the tube to be heated. The furnace is equipped with tap transformer, voltmeter, and pyrometer, and is capable of continuous operation at temperatures upwards of 1300° C.

The absorption train, *K*, *L*, *M*, *N*, is comprised of an unetched 250-ml. heat-resistant Erlenmeyer flask containing approximately 125 ml. of cool, freshly boiled distilled water, a Fleming gas-washing bottle containing concentrated sulfuric acid, followed by a U-tube containing magnesium perchlorate (Anhydrone), and a tared U-tube containing Ascarite and prepared in the conventional manner. It was experimentally established that with the concentrations of hydrogen fluoride involved, no loss occurs through either incomplete absorption in the single absorber or reaction with the glass.

Figure 2 shows the vaporizer in detail. The vial is approximately 7.5 cm. (3 inches) long and the bulb is blown to a volume of approximately 0.2 ml. The tip of the capillary is drawn or ground to an external diameter of 0.5 mm.

SAMPLE

A sample of not more than 40 to 60 mg. is taken. Volatile liquids are introduced into the weighed vial by warming the bulb gently, dipping the tip into the liquid, and allowing the sample to be drawn in as the bulb cools. *After filling*, the vial is maintained in an upright position and any excess sample is carefully expelled from the capillary portion by touching the latter momentarily with a warm rod. Solids and high-boiling liquids—i.e., those showing no measurable evaporation from an open container after 2 or 3 minutes on the balance pan—are weighed in a platinum boat.

PROCEDURE

Heat the furnace to a temperature of 1250° to 1275° C. and pass the water-saturated oxygen through the system at the rate of 30 ml. per minute. After several minutes connect the absorption train, adding 0.20 ml. of standard 0.1 *N* alkali and a few drops of phenolphthalein to the water in flask *K*. Gradually introduce the sample into the combustion zone according to either of the two methods given below, depending upon whether the material is volatile or not.

A. Volatile Materials. Adjust the position of the furnace so that it heats the center section of the combustion tube. Insert the vial into the 3-hole stopper, making a gas-tight seal. Gradually vaporize the sample into the oxygen stream by allowing a small droplet (4 to 5 mg.) to drop into the mixing chamber every 3 to 4 minutes. This is best done by touching the bulb momentarily with the hand or with a warm rod, so that the expanding vapor forces out the droplet. Very low-boiling liquids may volatilize from the tip of the capillary without forming a drop. In this case, control the rate of addition so that about 45 minutes are required to evaporate the sample completely. It is essential that this rate not be exceeded, for combustion may be incomplete or, in extreme cases, reaction with explosive violence may occur. The volatilization of materials boiling below about 60° C. is difficult to control and such materials cannot generally be analyzed by the described technique.

B. Nonvolatile Materials. Place the furnace so that it heats the portion of the combustion tube nearest the outlet end. Wrap the length of tubing extended from the furnace (about 35 to 40 cm.) with a layer of gauze and saturate the latter with water. Remove the plug and place the boat in the combustion tube at a distance of approximately 15 cm. from the open end. Immediately replace the plug and allow the oxygen to pass through for several minutes, then gradually remove the cooling wick. After 10 minutes move the furnace toward the sample at the rate of 1 cm. every 2 to 3 minutes until, by the decolorization of the phenolphthalein, it is evident that decomposition has begun. (The precautions against too rapid decomposition as indicated under (A) should also be followed in this instance.) Maintain the tube in this position for 20 minutes, then resume the controlled movement of the furnace until the sample is subjected to its full heat. Heat the portion of the tube between the side arm and the furnace to redness with a gas burner to ensure volatilization of any last traces of sample.

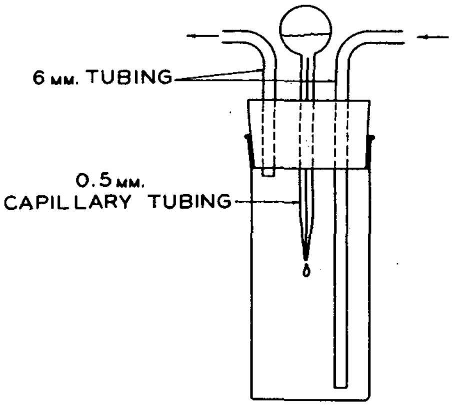

Figure 2. Vaporizer for Volatile Samples

Place the furnace so that the outlet end of the tube is again heated, and adjust stopcock *A* to permit dry oxygen to pass through the system. After 5 minutes disconnect the absorption train from the combustion tube and replace the stopper containing the platinum delivery tube by one fitted with a heat-resistant fritted-glass gas dispersion tube. Flush the acid solution for 15 minutes with a stream of oxygen or purified air to recover any dissolved carbon dioxide. Finally disconnect the U-tube, *N*, and weigh. The gain in weight represents the carbon dioxide formed by the combustion.

Table I. Determination of Fluorine and Carbon

Material	Theoretical, %		Found, %	
	Fluorine	Carbon	Fluorine	Carbon
o-Fluorotoluene[a]	17.26	...	17.2	..
p,p'-Difluorodiphenyl[b]	19.97	...	19.9	..
			19.5	
			20.0	
Benzotrifluoride[c]	39.01	...	38.4	..
			38.7	
			38.3	
Trifluoromethylbenzoic acid[d]	29.98	...	29.0	..
			30.6	
			30.0	
			29.9	
			30.0	
n-Perfluoroheptane[d]	78.33	...	78.6	..
			77.4	
Perfluoronaphthalane[d]	74.01	25.99	73.5	25.9
Perfluoromethylnaphthalane[d]	74.20	25.80	73.8	25.6
Perfluoro-*tert*-butylnaphthalane[d]	74.60	25.40	73.7	25.6
Perfluoromethylcyclohexane[d]	75.98	24.02	75.7	23.3

[a] Eastman Kodak No. 2967.
[b] Eastman Kodak No. 3281.
[c] Hooker Electrochemical Co.
[d] Material prepared in Socony-Vacuum Laboratories.

Titrate the acidic solution in the absorption flask to a phenolphthalein end point with 0.1 *N* alkali, adding to this titer the quantity of alkali originally added to serve as an indicator. The total is equivalent to the hydrofluoric acid resulting from the decomposition.

DISCUSSION OF RESULTS

Although no standard samples of fluorinated compounds were available, the method has been tested on a number of commercial and research materials (Table I). The commercial materials were used without purification. The research materials were indicated to be of relatively high purity by their physical constants, and, in the case of the completely fluorinated compounds, by the presence of only fractional percentages of residual hydrogen as determined by the pyrolysis method of Miller *et al.* (*4*). In general, agreement with the theoretical values for fluorine is good. Although a few comparatively low values were obtained, only in the case of the benzotrifluoride did the average of check determinations give an error amounting to as much as 1% of the amount present. In this instance, the low results were possibly due to the presence of a small amount of impurity, inasmuch as the material had been in the laboratory for some time prior to analysis and was no longer in the original container.

As the method was intended primarily for the determination of fluorine, only a few determinations were made for carbon. However, those results that were obtained for carbon are considered sufficient to indicate the wider applicability of the method.

No attempt was made to test the method in the presence of elements other than carbon, hydrogen, and oxygen. Other halogens or acid-forming elements would interfere with the direct alkalimetric titration of the fluorine as well as with the determination of carbon. In such instances, fluorine could possibly best be determined by a double titration technique (*4*) or by titration with thorium nitrate, whereas appropriate modification of the train would permit the simultaneous determination of carbon. In any event, the method would serve as a rapid means of decomposing the organic molecule and converting the fluorine into a readily determinable form.

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Spectrophotometric Determination of Osmium with Thiourea

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A spectrophotometric study has been made of the rose-red color produced when osmium(VIII) solutions are treated with acid and thiourea. The color develops rapidly and is stable. The system shows a moderately sharp transmittancy minimum at 480 mμ and a broad band, of slightly higher transmittancy, centering at about 540 mμ. The optimum concentration range for the method, when measurements are made against a reagent blank using a Beckman spectrophotometer at 480 mμ, is 8 to 40 p.p.m. In this range, the attainable accuracy is 2.9% relative error per 1% absolute photometric error, or about 0.6% relative error for a precision of 0.2% in making the photometric measurement. Of the other platinum metals, only palladium and ruthenium interfere, and then only when present in moderate amounts relative to the osmium present; a concentration of 20 p.p.m. of osmium will tolerate about 5 p.p.m. of palladium and 2 p.p.m. of ruthenium.

ALTHOUGH it has been nearly a century and a half since the discovery of the element osmium (1804), methods for its analysis have in general left much to be desired (*10*). Proposed methods have included: separation as sulfide followed by ignition in hydrogen; reduction of osmium(VIII) with alcohol and separation as hydrous oxide which is reduced in hydrogen; displacement from acid solution by active metals; precipitation as ammonium or potassium chloro-osmate; iodometric determination by reduction of osmium(VIII) with iodide (*6*); precipitation with strychnine sulfate (*9*); and potentiometric titration (*3, 4*).

The difficulties encountered in most of the previous methods can be eliminated by colorimetric analysis. Numerous color reactions of osmium have been reported. Chugaev (*2*) found that solutions of osmium tetroxide treated with thiourea and hydrochloric acid gave brilliant rose-red solutions due to the formation of $[Os(NH_2CSNH_2)_6]Cl_3OH$. Ogburn (*8*) listed about 60 reagents that give color reactions with osmium; however, most of these reactions give precipitates and are therefore unsuitable

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for colorimetry. Steiger (*12*) studied reactions of 21 compounds of the general formula $(R_2N)_2CS$ with osmium and ruthenium, and showed the dependency of color formation on the $=C=S$ group linked to one or two $-NH_2$ or $-NHR$ groups. Yoe and Overholser (*13*) tested 60 substituted thioureas with 78 inorganic ions, and in general found that the substituted thioureas offered little or no advantage over the parent compound. The thiourea color reaction was used by Sandell (*11*) in determining traces of osmium in meteorites; the measurements were made with a photoelectric photometer using a green filter.

The purpose of the present investigation is to make a detailed spectrophotometric study of the osmium-thiourea system, particularly with reference to evaluation of optimum range and maximum accuracy, and also to determine the nature and extent of possible interference from other platinum metals.

REAGENTS

Osmium tetroxide, C.P., in sealed glass ampoules, was obtained from the Fisher Scientific Co.

Test solutions of rhodium(III), palladium(II), iridium(IV), and platinum(IV) were prepared from their C.P. chlorides. Ruthenium test solution was prepared by dissolving C.P. ruthenium metal in alkaline hypochlorite, followed by acidification and boiling to remove chlorine; this process is reported to give ruthenium(III), or a mixture of ruthenium(III) and ruthenium (IV) (*7*). In order to prevent reduction by contact with organic matter (cork, rubber stoppers), all test solutions of the platinum metals were stored in glass-stoppered containers.

Thiourea, 10% aqueous solution, was prepared from the Eastman Kodak Company product.

Sodium thiosulfate solution was standardized against potassium iodate.

APPARATUS

Transmittancy measurements were made with a Beckman model DU quartz spectrophotometer, using Corex cells 1.004 cm. thick for the visible range, and silica cells 1.000 cm. thick for a few measurements in the near ultraviolet. The instrument was operated at constant sensitivity, using slit widths of the order of 0.02 to 0.10 mm., corresponding to nominal band widths of about 1 to 4 millimicrons.

EXPERIMENTAL

Preparation and Standardization of Osmium Solution. A 1-gram ampoule of osmium tetroxide was scratched with a file, weighed, and broken beneath the surface of about 100 ml. of 0.2 *M* sodium hydroxide contained in a glass-stoppered flask. The red-orange solution was washed into a 1-liter volumetric flask and made up to volume with distilled water. Recovery and weighing of the broken glass gave the weight of osmium tetroxide by difference.

Attempts to standardize the osmium solution by the strychnine sulfate method (*9*) were unsuccessful. In this method the alkaline solution of osmium tetroxide is first converted to the chloroosmate by treatment with a small amount of ethyl alcohol followed by acidification with hydrochloric acid and boiling; a clear yellow solution should result. Several trials using varying amounts of ethyl alcohol and/or hydrochloric acid always produced a solution which was yellowish brown to nearly black. Precipitation with strychnine sulfate gave gray precipitates rather than the canary-yellow precipitate described in the method; the results, calculated to osmium, were not quantitatively precise and were always too low based on the weight of osmium tetroxide taken.

The iodometric method of Klobbie (*6*) was used successfully. A 25.0-ml. aliquot of the stock solution was treated with 15 ml. of 6 *M* sulfuric acid and 2 grams of potassium iodide; the liberated iodine was titrated with 0.02510 *N* sodium thiosulfate. The reported difficulty of determining the end point, on account of the green color of the reduced osmium, was circumvented by use of the starch indicator externally. Quadruplicate titrations gave the following results:

Osmium, mg./liter	737.6, 737.6, 739.1, 739.6
Av.	738
Calculated to OsO_4, mg./liter	986
Weight of OsO_4 taken, mg.	1004

Measurement of Transmittancy. Solutions containing suitable increments of osmium from 1 to 200 p.p.m. were prepared as follows:

The calculated volume of stock solution was measured into a 100-ml. volumetric flask containing about 50 ml. of distilled water; 10 ml. of 6 *M* sulfuric acid and 1 ml. of 10% thiourea solution were added and the sample was made up to volume with distilled water. The blank solution contained the reagents in the same amounts.

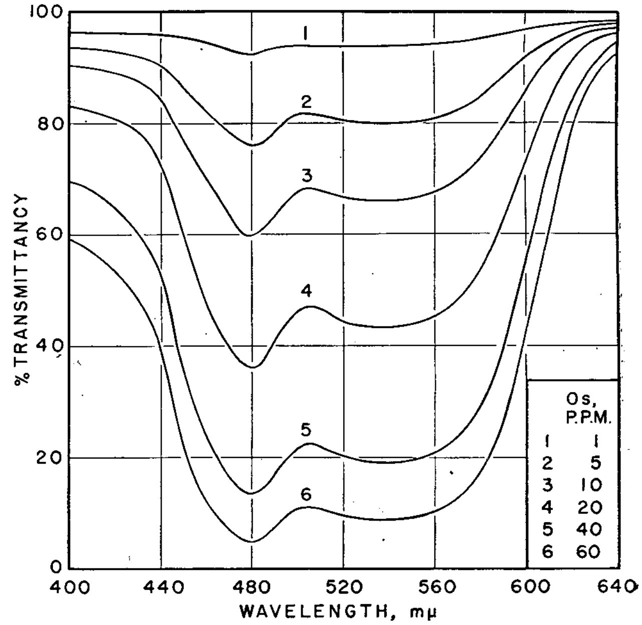

Figure 1. Spectral Transmittancy Curves for Osmium with Thiourea

Data for transmittancy–wave-length curves were obtained by measuring the transmittancy, against the reagent blank, at 10-, 5-, or 2-mμ intervals over the range 640 to 400 mμ. The solutions varied in osmium concentration from 1 to 100 p.p.m. Some typical transmittancy–wave-length curves are shown in Figure 1. All curves have minimum transmittancy at 480 mμ and a very broad, flat region of slightly higher transmittancy centered at about 540 mμ. Below 400 mμ the transmittancy again decreases sharply; however, measurements below 340 mμ are of little significance because thiourea itself shows strong absorption below about 340 mμ (*5*), the solution becoming optically opaque at 280 mμ, where it becomes impossible to balance the instrument for the blank even by maximum slit width (2.0 mm.) and adjustment of the sensitivity control.

The absorption by solutions more concentrated than 100 p.p.m. was too great to be measured accurately against a reagent blank, but could be measured by the differential method (*1*) against a slightly less concentrated osmium-thiourea standard solution.

A plot of log transmittancy against concentration showed good conformity to Beer's law over the range of concentrations measured (up to 100 p.p.m.); Sandell (*11*) has reported conformity to Beer's law for this system in the low concentration range (up to 3 p.p.m.).

Rate of Color Development. Measurements of transmittancy against time showed that the color developed very rapidly during the first 5 minutes, and reached a stable value in less than 10 minutes, at room temperature (32° C.). More rapid color development can be made by warming the mixture, but is scarcely necessary. Sandell (*11*) reported full color development in less than 5 minutes with solutions containing up to 3 p.p.m.

Stability of Color. Solutions of various concentrations of osmium with thiourea showed no measurable change in transmittancy at 480 mμ over a period of 8 days; several solutions measured after 19 days were unchanged.

Effect of Temperature. At 480 mμ, solutions containing 10 to 20 p.p.m. of osmium showed an increase in transmittancy of 0.1%

(absolute) per 1° C. temperature rise in the range 25° to 45° C. The temperature effect is completely reversible.

Interference from Other Platinum Metals. The tests reported by Ogburn (*8*) for the reaction of thiourea with solutions of the platinum metals would indicate that interference might be expected from ruthenium, rhodium, and platinum, but not from palladium nor iridium; however, Yoe and Overholser (*13*) found that palladium(II) gave a yellow color with thiourea. Qualitative tests on separate solutions of each of the other platinum metals in acid solution showed no reaction with thiourea in the cases of rhodium, iridium, and platinum; palladium produced a yellow color; the ruthenium-thiourea mixture was yellow at first (color of the ruthenium test solution), changing within a few minutes to pale amber, then, in about 0.5 hour, to light greenish blue; the blue color slowly increased in intensity over a period of several days. The ruthenium-thiourea mixture developed to a stable intense greenish-blue color almost immediately upon heating to boiling.

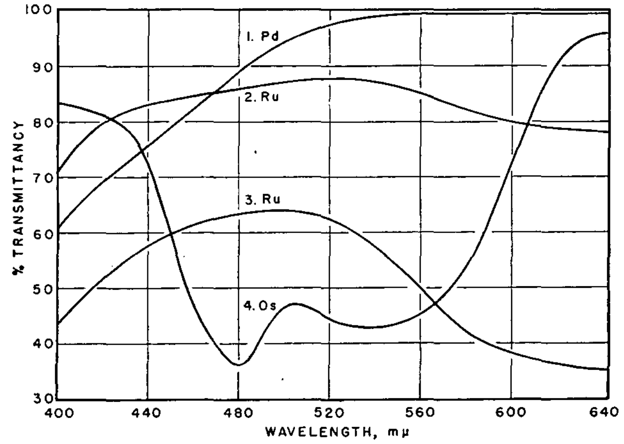

Figure 2. Spectral Transmittancy Curves for Thiourea Systems

All solutions, 20 p.p.m. of metal

1. **Palladium**
2. **Ruthenium, developed at room temperature**
3. **Ruthenium, developed by heating to boiling**
4. **Osmium**

The spectral curves, from 640 to 400 mμ, for thiourea with palladium, ruthenium, and osmium, each at 20 p.p.m., are shown in Figure 2. During the first half hour the transmittancy of the ruthenium solution which was developed at room temperature was much smaller in the low wave-length range and somewhat larger in the high wave-length region than shown in curve 2, but the transmittancy was changing so rapidly that accurate readings were impossible. Readings for curve 2 were started about 0.5 hour after preparation of the sample; because the transmittancy was still changing, although more slowly, curve 2 is approximate only. Curve 3 is for the ruthenium solution developed by heating the mixture to boiling. The shapes of the spectral curves indicate that palladium and ruthenium in moderate amounts would interfere with the determination of osmium at 480 mμ. In order to determine the extent of this interference, solutions containing 20 p.p.m. of osmium and varying amounts of palladium or ruthenium were measured at wave lengths between 580 and 400 mμ. The tolerance of the osmium-thiourea system for the interfering substance was taken as the largest amount of the latter that would give a transmittancy not more than 0.4% (absolute) different from that of the osmium alone. This limit was set on the assumption that replicate determinations on a given solution can be reproduced to 0.2% absolute transmittancy—a precision which is not difficult to realize. On this basis the osmium-thiourea system can tolerate up to about 5 p.p.m. of palladium (25% of the amount of osmium present) at any wave length between 580 and 480 mμ; below 470 mμ, interference from palladium becomes very pronounced. The tolerance for ruthenium on samples developed at room temperature is about 2 p.p.m. (10% of the amount of osmium present) at 480 mμ, but this amount of ruthenium gives serious interference at wave lengths near 580 mμ and below 460 mμ. Reference to curve 3 of Figure 2 shows that interference from ruthenium would be much more extensive if samples were heated before measuring the transmittancy.

DISCUSSION

The calibration curve for the determination of osmium with thiourea is shown in Figure 3, in which per cent absorptancy—i.e., 100 − % transmittancy—at 480 mμ is plotted against log concentration. The advantages of this method of plotting photometric data have been discussed fully elsewhere (*1*). From Figure 3 it is obvious that the optimum concentration range for the method is approximately 8 to 40 p.p.m.; in this range the relative analysis error is 2.9% per 1% absolute photometric error, which is very close to the theoretical limit (2.7% relative error) imposed by Beer's law. For a precision of 0.2% absolute in transmittancy measurements, the minimum relative error of the photometric process is 0.6% of the concentration represented. If desired, the range could be extended upward and the accuracy increased by the use of the differential method. In the concentration range 1 to 3 p.p.m. (*11*) the relative analysis error is about 12% per 1% absolute photometric error, or about 2.5% for 0.2% precision in transmittancy measurement.

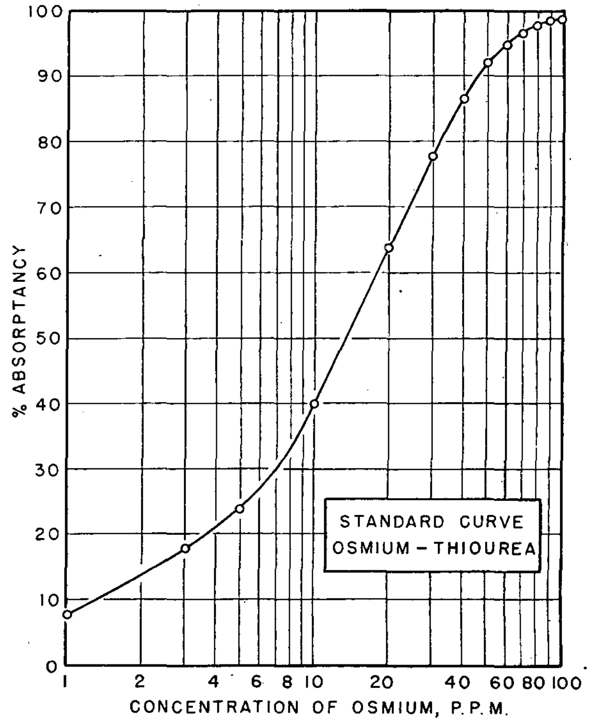

Figure 3. Calibration Curve for Osmium with Thiourea at 480 mμ

A curve plotted from the 540 mμ transmittancies is parallel to the 480 mμ curve shown in Figure 3 but is displaced slightly to the right; such a curve covers essentially the same optimum concentration range. Use of the 540-mμ curve in analysis might have some advantages over the 480-mμ curve: The broad, flat shape of the curve around 540 mμ would require little care in making the setting of the wave-length scale; at 540 mμ, palladium up to 20 p.p.m., and probably much higher, does not interfere (see Figure 2, curve 1); however, interference from ruthenium at 540 mμ is approximately the same as at 480 mμ (see Figure 2, curve 2).

The temperature coefficient of transmittancy of the osmium-thiourea system is so slight that no difficulty is encountered from temperature variations of a few degrees.

The tolerance of the osmium-thiourea system for moderate amounts of ruthenium is particularly fortunate, in that a very sharp separation of ruthenium from osmium would not be required.

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Spectrographic Determination of Potassium in Iron Catalysts by Fractional Distillation

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A spectrographic method for the determination of potassium in iron catalysts has been developed. Potassium was found to distill quantitatively from a sample pellet during the initial arcing period. By photographing the spectrum during this period only, interference due to iron was eliminated. The length of the log sectored potassium line was found to be a linear function of the log concentration of potassium. An average deviation of from 5 to 10% of the amount present is indicated by repeated determinations on the same sample. Sodium and lithium can be determined in the same manner.

IRON catalysts containing potassium are important in ammonia and Fischer-Tropsch syntheses. There may be a tendency for some of the potassium to be volatilized during the preparation of the catalyst, so that the final concentration of potassium is somewhat uncertain. Wet chemical methods for the determination of potassium are tedious; hence a spectrographic method was sought.

Potassium has a spectrum relatively poor in sensitive lines in the region of the visible and ultraviolet. The sensitive lines available are the doublets of the fundamental series of which the red lines of wave lengths 7699.0 and 7664.9 Å. are the first and hence strongest members. However, because photography in this region is not very convenient and the lines are subject to strong self-reversal, the second or third members in the series are used more frequently—namely, the violet lines of wave lengths 4044.2 and 4047.2 Å., and the ultraviolet of 3446.4 and 3447.4 Å., respectively. The violet lines straddle the strong iron line at 4045.8 Å.; thus they are easily masked in the case of the type samples under consideration. The ultraviolet lines in general do not have sufficient sensitivity. The problem thus resolved itself into one of maintaining or increasing the sensitivity of potassium lines while reducing that of iron lines (and of carbon if carbon electrodes were to be used).

In experimenting with various excitation conditions it was observed that when a low current, direct current arc was used the sample burned in two stages. At first the arc was almost invisible and burned quietly. After a time it changed suddenly to the characteristic blue color of an iron arc accompanied by a slight hissing sound. The temperature of the sample increased rapidly as this point of change was approached until it formed a molten bead. Moving plate studies showed that during the first period few lines other than those due to potassium appeared, whereas during the latter period the potassium lines were absent and those of iron and other constituents were excited. Thus potassium was distilled from the catalyst almost completely before the spectrum of iron was excited. The total energy of the potassium lines was found to be a function of the concentration of potassium. Therefore, in the procedure developed, arcing was continued just long enough to volatilize all the potassium—i.e., until the arc assumed a blue color. The principle described is essentially that of the "total energy" method advocated by Slavin (*2*), and in some respects similar to the "carrier distillation" method for the analysis of uranium ores developed by Scribner and Mullin (*1*).

EXPERIMENTAL

A summary of the experimental conditions under which spectra were obtained is given in Table I.

The sample pellet was chosen to be large enough to handle conveniently but small enough so that the arcing time was not excessive. For the concentration range above 0.25%, the sample

Table I. Experimental Conditions

Sample	0.100 gram $^5/_{32}$-inch diameter cylindrical pellet, grain size to pass 140-mesh
Spectrograph	21-foot Jarrell-Ash grating
Spectral region	Second order 4000 Å.
Filter	Corning No. 774
Optical system	19.7-cm. focal length plano-convex lens on slit, source 21.5 cm. from slit
Slit width	30 microns
Lower electrode	0.25-inch carbon with flat end to support pellet
Upper electrode	0.125-inch graphite, pointed
Gap	Maintained at approximately 0.5 mm.
Multisource	C = 60 mfd., L = 560 μh, R = 300 ohms
Voltage	Primary 230, secondary 940
Arc current	2.5 amperes
Polarity	Pellet made positive
Exposure	Until 5 seconds after arc changed
Emulsion	Eastman spectrum analysis No. 1
Development	2 minutes in D-19, 20° C., mechanical agitation
Density calibration	Rotating logarithmic spiral sector
Analysis line	K 4047 Å.

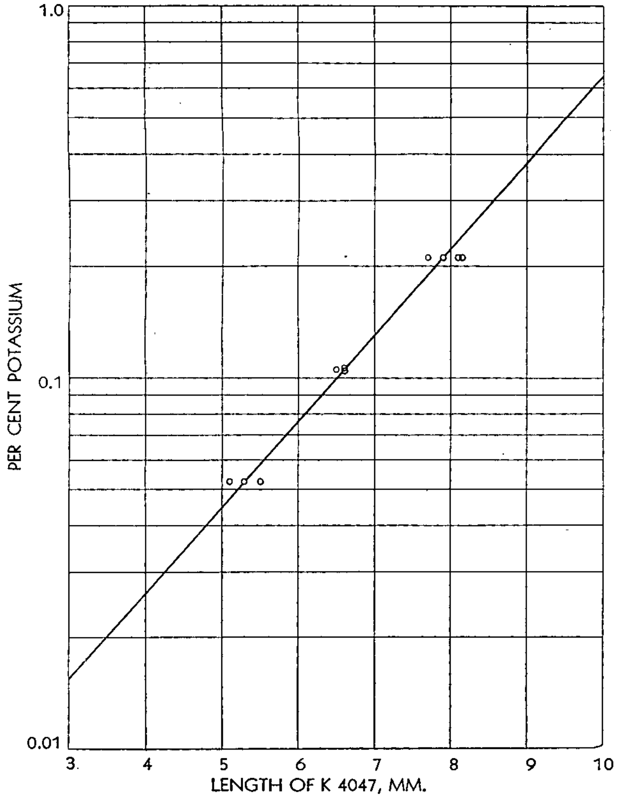

Figure 1. Working Curve for Potassium

was diluted with a pure iron oxide sample prepared in the same way as the catalysts but without potassium. This concentration required an arcing time of about 2 minutes. The pointed upper electrode and small gap were chosen to keep the arc centered on the pellet itself. The flat-end lower carbon electrode served simply as a conducting support for the pellet. No significant differences in results were obtained, however, when graphite was used in place of carbon.

The condenser lens and source were so positioned that an image of the arc was thrown on the collimating mirror of the large Jarrell-Ash grating spectrograph. The second-order spectrum was used because of the greater dispersion and because the intensity of distribution along spectral lines was most nearly uniform in this region. The logarithmic spiral sector was rotated as close to the slit as possible.

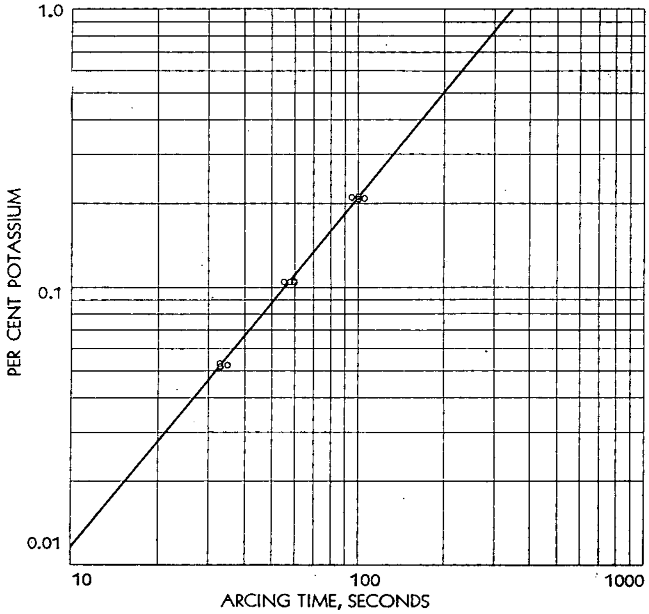

Figure 2. Working Curve for Potassium Using Arcing Time

The lengths of the wedge-shaped lines were measured as projected on the screen of an Applied Research Laboratories densitometer-comparator with a magnification of over 20 times.

A specially prepared catalyst was analyzed by the well known chloroplatinate method to provide a standard for spectrographic work. (The chemical value of 0.21% potassium in this sample was used throughout this work. A flame photometer analysis gave the result as 0.26% based on synthetically prepared potassium standards.) This standard was diluted with the pure iron oxide as previously described to make a working curve (Figure 1). However, because no internal standard was used, several spectra of the standard catalyst were usually included with a set of analyses to check the work curve. A working curve was also made which relates the arcing time required to volatilize the potassium as a function of the concentration of potassium (Figure 2). This is a convenient rough check, but is not as reliable, because the presence of other alkalies will increase the time required.

Table II. Analyses of Some Iron Catalysts

Catalyst	% K, Repeated Determinations	Average % K	% Average Deviation	% K from Time Curve
Magnetite ore	0.26, 0.21, 0.24, 0.21, 0.24, 0.20	0.23	9	0.34[a]
76	1.4, 1.3, 1.4	1.4	2	1.2
108-7	0.20, 0.18, 0.22, 0.25, 0.24, 0.21, 0.24, 0.20	0.22	12	0.22
108-7 (reduced)	0.12, 0.14, 0.12, 0.12, 0.11, 0.11	0.12	6	0.14
122-1	0.75, 0.72, 0.74, 0.72, 0.69, 0.80, 0.80	0.75	4	0.84[a]
122-1 (reduced)	0.74, 0.70, 0.68, 0.65, 0.74, 0.72	0.70	4	0.80[a]
207	0.02, 0.035	0.03	..	0.04

[a] Magnetite ore was used as starting material for 122-1 and contains about 0.15% sodium; hence, the apparent per cent potassium as determined from the time of arcing is high.

RESULTS

The analyses of several catalysts are given in Table II. A number of repeat determinations are given in each case to show what reproducibility is attained. The reported values include both those for which the sample was arced as received, and those for which the sample was diluted.

The agreement in general is good between the potassium concentration determined from the length of lines and from arcing time. The samples whose time values are high were found to contain about 0.15% sodium, which behaves in a similar manner in the arc. Most samples contained a trace of sodium (usually less than 0.01%) including the standard.

The method described is applicable down to about 0.01% potassium. For lower values it is usually not possible to observe the initial arcing period during which only potassium is volatilized. A definite upper limit was not established, but an analysis (without dilution) can be made for samples having up to 1.5% potassium—for example, the direct analysis of a commercial ammonia synthesis catalyst (No. 76 in Table II) gave consistent results with that obtained upon dilution of the catalyst to one tenth its original concentration of potassium. However, the arcing time of nearly 8 minutes would be inconveniently long for routine analysis.

DISCUSSION

The method described here is not applicable to catalysts containing several per cent of carbon. Such samples burned erratically and did not have an initial period during which only potassium was volatilized. Catalysts that have been used in hydrocarbon synthesis will generally have enough carbon deposit to behave in this way. Reduced catalysts may be analyzed, although there is a slight sputtering at the outset. (The oxide when treated with hydrogen is reduced to the metallic state.

Any subsequent exposure to air results in a partial oxidation. Thus the reduced catalysts which are analyzed are not fully reduced.) A lower arc current would be preferable in this case.

No serious attempt was made to find a suitable internal standard in applying this method because the accuracy attained otherwise was deemed satisfactory. Obviously the major constituent, iron, is not a satisfactory standard. Elements found to behave in the same way as potassium were sodium and lithium when added to the iron catalyst. Neither has lines in the immediate neighborhood of the violet potassium lines, but they could possibly be used. Sodium would be less desirable because it occurs as a variable impurity in the samples. Lead and calcium have lines favorably located, but, although they are excited, they are not completely exhausted during the initial arcing period.

The possibility of using the arcing time as a measure of the concentration of potassium is intriguing because of its simplicity. The apparatus required is a stop watch, a controlled direct current arc source, and means for making the sample pellets. The analysis may be performed in a few minutes. The presence of appreciable quantities of sodium (or lithium) could readily be detected by the color of the discharge, and hence such samples could be analyzed spectrographically. Because sodium and lithium behave in the same manner as potassium, a spectrographic analysis may be made simultaneously for the three elements.

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Chromatographic Estimation of Carotene in Feeds and Feed Ingredients

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A rapid method for the estimation of chromatographic carotene in alfalfa meal, corn, corn products, and finished feeds is described. The use of a combination of three solvents (toluene, ethyl alcohol, and ethyl acetate) results in improvement in the completeness of extraction of carotenoid pigments. The method estimates the total concentration of all the known vitamin A–active carotenoids.

A NUMBER of methods for the extraction of carotene from alfalfa meal have been proposed.

Wall and Kelley (*11*) recommend refluxing the sample for 0.5 hour with 30% acetone and 70% Skellysolve B. The tentative Association of Official Agricultural Chemists procedure (*2*) is essentially a modification of this method but uses a 1-hour reflux time. The extraction method of Silker *et al.* (*9*) is to shake the sample with 1 part of acetone and 2 parts of Skellysolve B in a tightly stoppered container, after which the mixture is allowed to stand in the dark for 16 to 18 hours. Although the A.O.A.C. phasic method (*3*) for carotene (crude carotene) is no longer official, provision is made (*1*) for extraction of carotene from alfalfa meal and similar materials by refluxing with 12% alcoholic potassium hydroxide solution for 30 minutes. No specific A.O.A.C. recommendation has been made for extraction of pigments from yellow corn and corn products such as corn gluten meal and corn gluten feed. However, Buxton (*4*) suggests refluxing ground yellow corn for 1 hour with 5% methanolic potassium hydroxide, and Fraps and Kemmerer (*5*) recommend 12% alcoholic potassium hydroxide (30 minutes) for extraction of pigments from ground yellow corn.

The authors propose the use of a mixture of equal parts of toluene, ethyl alcohol, and ethyl acetate for the extraction of carotenoids and other pigments from plant materials. After the sample is refluxed with the solvent mixture, the solvents are evaporated and the pigments are dissolved in petroleum ether (Skellysolve B). This solution of pigments is passed through a magnesia–Hyflo Super-Cel adsorption column and the carotene is eluted from the column by means of 10% acetone in Skellysolve B.

As compared with boiling in 12% alcoholic potassium hydroxide, refluxing alfalfa meal with 30% acetone in Skellysolve B (tentative A.O.A.C. method) is a good method for extracting the carotene (Table I). Apparently, however, the proposed solvent mixture more completely extracts the carotene than does the 30% acetone (Table II). Furthermore, the tentative A.O.A.C. extraction is not applicable to corn and corn products nor to manufactured feeds (Table III). Refluxing a variety of dried plant materials with 12% alcoholic potassium hydroxide according to the formerly official A.O.A.C. crude carotene method appeared to be the most effective procedure until this work on the new solvent

Table I. Extraction of Carotene

Sample	Crude Carotene, Phasic Method, γ/G.	Chromatographic Carotene, γ/Gram: Alcoholic potash through magnesia	Chromatographic Carotene, γ/Gram: Tentative A.O.A.C. chromatographic method[a]
Dehydrated alfalfa meal A (over 1 year old)	45.4	36.0	37.6
Dehydrated alfalfa meal B (fresh)	206.0	190.0	195.0

[a] Extraction with 30% acetone in Skellysolve B for 1 hour.

Table II. Chromatographic Extraction of Carotene

Sample	Tentative A.O.A.C. Method	Proposed Method	
	γ/g.	γ/g.	
Dehydrated alfalfa meal A[a]	37.6	40.3	
Dehydrated alfalfa meal B[a]	195.0	210.9	
Dehydrated alfalfa meal C	38.5	43.0	
Western sun-cured alfalfa meal	14.5	17.0	
		Additional Carotene in Residue[b]	
		γ/g.	% of total
Dehydrated alfalfa meal	38.5	4.3	10.0
Western sun-cured alfalfa meal	14.5	1.5	9.4

[a] Same sample as in Table I.
[b] Residue from 30% acetone extraction re-extracted with proposed solvents mixture.

Table III. Extraction of Carotene

Sample	Tentative A.O.A.C. Method	Proposed Method
	γ/g.	γ/g.
Corn gluten meal	2.0	27.0
Corn gluten feed	0.8	5.6
Ground yellow corn	0.4	2.4
Poultry mash	1.2	3.4

Table IV. Extraction of Carotene by Three Different Methods

Sample	Crude Carotene, Phasic Method	Chromatographic Carotene, Alcoholic Potash through Magnesia	Proposed Method
	γ/g.	γ/g.	γ/g.
Corn gluten meal	40.0	14.5	19.4
Corn gluten feed	7.5	3.3	4.2
Ground yellow corn	4.0	2.0	2.0
Poultry mash[a]	10.0	6.1	8.6
Dehydrated alfalfa meal (6 months old)	114.1	86.2	113.9
Dehydrated alfalfa meal (fresh)	174.2	141.0	185.9

[a] Contains ground yellow corn, wheat bran, wheat middlings, ground oats, ground barley, corn gluten meal, soybean oil meal, dehydrated alfalfa meal, meat scraps, fish meal, and dried milk products.

was developed. Table IV indicates that the alcoholic potassium hydroxide extraction is not as efficacious as previously thought.

PROPOSED PROCEDURE

Reagents. Petroleum ether. Skellysolve B is recommended.

Eluting reagent, 10% acetone in petroleum ether.

Anhydrous sodium sulfate.

Adsorbent prepared from an equal mixture by weight of activated magnesia and diatomaceous earth. The authors have used successfully Micron Brand No. 2641 magnesia manufactured by Westvaco Chlorine Products Corporation, Newark, Calif., and Johns-Manville Hyflo Super-Cel.

Solvent mixture made up of equal parts by volume of toluene, ethyl acetate, and 95% ethyl alcohol, all reagent grade.

Apparatus. Fat extractor. A Goldfisch, Bailey Walker, or Soxhlet extractor is suitable.

Spectrophotometer. A Coleman Model 11 was used in this work and confirming data were obtained using a Beckman DU spectrophotometer.

Preparation of Adsorption Column. Use a chromatographic tube which has a barrel 23 mm. in diameter and 200 mm. long. Prepare the adsorption mixture by rubbing out lumps and rolling the ingredients on paper at least 50 times. An ordinary kitchen flour sifter has been found helpful in dispersing lumps in the adsorbent. Place a small plug of cotton in the bottom of the tube and pack the absorbent firmly into the tube to a depth of 100 mm., applying suction during the process. Superimpose on the adsorbent a 1-cm. layer of anhydrous sodium sulfate. It is unnecessary to wet the column with solvent prior to use.

Procedure. The sample should pass a 40-mesh screen. Weigh 1 gram of dehydrated alfalfa meal or 5 grams of corn, corn gluten meal, or a feed mixture into the solvent reservoir of a fat-extraction flask. Add 50 ml. of the solvent mixture and reflux on the extractor for 60 minutes.

Remove the solvent flask from the extractor and cool. Filter the contents of the extraction flask with suction, collecting the solution of plant pigments in a 250-ml. Erlenmeyer flask. Connect the flask to a water pump and evaporate the solvents under reduced pressure while shaking the flask in a beaker of water heated to 70° to 80° C. Dissolve the residue in 25 ml. of 10% acetone in Skellysolve B and pass this solution through the adsorption column under suction.

Elute the carotene from the column, using 50 to 75 ml. of 10% acetone in Skellysolve B. Use the first 25 ml. of eluent to rinse the Erlenmeyer flask and pour the rinsings through the column.

Place eluate in a 50-ml. volumetric flask and make up to volume with 10% acetone solution. Determine carotene spectrophotometrically at 440 mμ wave length, comparing results with those obtained using a standard solution of pure β-carotene, or of 10% α–90% β-carotene purified by precipitation with methanol (*3*).

Frequently in a feed products control laboratory a rapid method is necessary for the estimation of the carotene content of incoming alfalfa meal and other ingredients, whereby numerous samples may be assayed without sacrificing too much accuracy. Although the alternative method suggested below is inherently not as precise as the above proposed procedure, very comparable and reliable results (Table V) can be obtained with it if recommended precautions are taken.

ALTERNATIVE RAPID PROCEDURE

The reagents are the same as in the proposed procedure (above).

Apparatus. The same apparatus is used, plus a graduated 100-ml. lipless cylinder. The chromatographic tubes are 23 × 200 mm. cylinders sealed to 4 × 80 mm. tubes.

Pass the stem of the chromatographic tube through a two-hole stopper of proper size to fit in the top of the 100-ml. lipless graduated cylinder. Through the other hole in the stopper insert a bent glass tube and connect this to a source of vacuum. Ordinarily an efficient water pump will suffice, but a rotary vacuum pump is advantageous. Where volume of work is large, a battery of six of these chromatographic assemblies may be used by connecting each assembly to a suction manifold by means of individual brass stopcocks.

The adsorption column is prepared in the same way as in the proposed procedure.

Rapid Procedure. Grind the sample if necessary until it will pass a 40-mesh screen. Weigh 1 to 2 grams of dehydrated alfalfa meal or 5 to 10 grams of corn, corn gluten meal, or feed into the solvent reservoir of a fat-extraction flask. Add exactly 50 ml. of the solvent mixture and carefully mark the level of the liquid in the flask with a fine pointed china marking pencil. Reflux on the extractor for 60 minutes.

Remove the solvent flask from the extractor, stopper with a suitable cork, and cool. Add sufficient solvent mixture from a pipet to bring the level of the liquid in the flask to the pencil mark and mix. Again stopper and allow to settle. Pipet 25 ml. of the supernatant extract into a 25-ml. Erlenmeyer flask, connect the flask to a water pump, and evaporate the solvents under reduced pressure while shaking the flask in a beaker of water heated to 70° to 80° C. Dissolve the residue in 25 ml. of 10% acetone in Skellysolve B and pass this solution through the adsorption column under suction. Elute the carotene from the column, using 50 ml. of 10% acetone in Skellysolve B. Use the first 25 ml. of eluent to rinse the Erlenmeyer flask, and pour the rinsings through the column.

Collect eluate in the 100-ml. lipless graduated cylinder. Disconnect the cylinder from the adsorption column, make up to the 50-ml. mark with 10% acetone solution, and mix. Determine carotene spectrophotometrically according to the proposed procedure.

Table V. Extraction of Carotene by Proposed Method and Alternative Rapid Method

Sample	Proposed Method	Alternative Rapid Method
	γ/g.	γ/g.
Poultry mash	4.0	4.2
Hog feed	5.0	5.0
Corn gluten meal	20.6	22.0
Corn gluten feed	4.4	4.6
Ground yellow corn	2.2	2.4
Mixture of sun-cured and dehydrated alfalfa meals	35.4	35.4

EFFECT OF SAPONIFICATION

The following procedure was used to provide information on the effect of saponification before chromatographing.

After extraction by the proposed procedure filter off the extracts and evaporate the solvents. Saponify the residue by refluxing 30 minutes with 25 ml. of 12% alcoholic potash. Allow to cool and add 25 ml. of water. Pour solution into a 125-ml. separatory funnel. Extract carotene and other pigments by shaking with 25-ml. portions of Skellysolve B (four extractions). Combine the four 25-ml. portions of Skellysolve B and wash three times with 50 ml. of water each. Dry Skellysolve B extracts by passing through anhydrous sodium sulfate.

Pass the nonsaponifiable fraction through a magnesia–Super Cel adsorbent column and elute according to the proposed procedure.

Table VI. Effect of Saponification on Extracts before Chromatographing

Sample	Carotene, Proposed Method Without saponification	 With saponification
	γ/g.	γ/g.
Corn gluten meal	27.0	26.2
Corn gluten feed	5.6	5.2
Ground yellow corn	2.4	2.0
Poultry mash	3.4	3.6
Dehydrated alfalfa meal	43.0	42.0
Western sun-cured alfalfa meal	17.0	16.0

Table VI shows the effect of saponification on the extracts before chromatographing. In some cases saponifying the extracts before passing them through an adsorption column appears to lower results slightly; this may be attributed to some losses incurred by manipulation during saponification and subsequent phasic extraction.

ISOMERIZATION

In all methods for the determination of carotene where thermal treatment is involved, isomerization of the carotene may take place (*6*) with formation of neo-β-carotenes from alfalfa meal, and in the case of corn and corn products possibly neocryptoxanthin and neo-α-carotene (*5*). The recommended solvent mixture of equal volumes of toluene, ethyl acetate, and ethyl alcohol has a boiling point of 74° C., which is somewhat higher than the boiling point of Skellysolve B (67° C.) and pure hexane (69° C.). Kemmerer and Fraps (*7*), verifying the work of Polgar and Zechmeister (*8*), prepared neo-β-carotene B by refluxing crystalline carotene with hexane for 1 hour.

By inference, heating for 1 hour at the boiling point of the authors' proposed solvent mixture should also cause isomerization of the carotene. Likewise, even refluxing with 30% acetone in Skellysolve B (boiling point of this mixture is 54° C.) for the above period should produce some isomeric change in the provitamin A pigments.

In order to investigate the effect of thermal treatment on carotene by the proposed method, various solutions including pure β-carotene and neo-β-carotenes U and B were prepared and separated by the method used by Kemmerer and Fraps (*7*), employing calcium hydroxide as adsorbent. Carotene solutions from alfalfa meal were prepared according to the tentative A.O.A.C. chromatographic carotene method, and carotene solutions from the same samples of alfalfa meal were prepared by the procedure proposed in this paper.

A Beckman DU spectrophotometer was used to obtain light absorption curves on these solutions for the purpose of comparison and identity.

Figure 1 presents the absorption curve of pure β-carotene as compared with curves of carotene solutions from a sample of dehydrated alfalfa meal, one of which was obtained by the 30% acetone in Skellysolve B extraction and the other by the solvent mixture extraction. Both were chromatographed with magnesia–Super Cel adsorption columns. From the shapes of the curves and the maxima of 451 and 478 mμ it is evident that the proposed procedure produces carotene solutions which have spectroscopic characteristics very similar to the solutions obtained by the tentative A.O.A.C. method.

No extensive work was done to determine and separate quantitatively all the isomers of carotene formed using the solvent mixture. However, extracts from alfalfa meal using the proposed method of extraction were subjected to chromatographic analysis on calcium hydroxide. Besides β-carotene (maxima in Skellysolve B 451 and 478 mμ), neo-β-carotene U (443 and 468 mμ) and neo-β-carotene B (446 and 473 mμ) were separated and identified.

Although the formation of carotene isomers due to heat during extraction has been demonstrated, the effect of this isomerization may be eliminated or at least mitigated to a great extent by taking readings at 436 mμ on a Beckman spectrophotometer, because at this wave length β-carotene and most of its isomers have practically the same specific absorption coefficients. Data in Tables III, IV, V, and VI were obtained using the Beckman instrument at 436 mμ (pure β-carotene as standard) and in Tables I and II using a Coleman Model II spectrophotometer at 440 mμ (purified 90% β–10% α-carotene as standard). Values in Tables I and II were also checked using the Beckman.

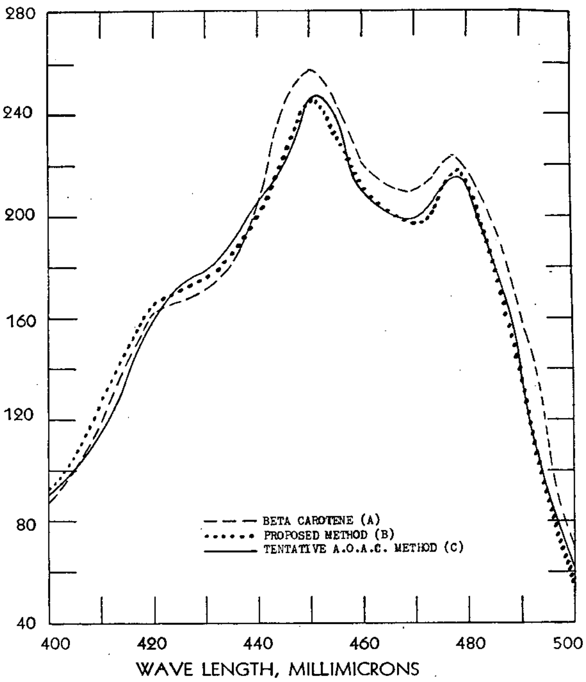

Figure 1. Comparison of Light Absorption Curves

A. Pure β-carotene dissolved in 10% acetone in hexane
B. Carotene solution from alfalfa meal by proposed method
C. Carotene solution from alfalfa meal by A.O.A.C. method

According to Strain (*10*) and Zechmeister and Cholnoky (*14*) cryptoxanthin, when subjected to chromatographic separation, is more strongly absorbed than α- and β-carotene and even lycopene. The fact that cryptoxanthin is a major vitamin A–active pigment in yellow corn and corn products necessitated an investigation as to whether it passes through the magnesia–Super Cel column by elution with 10% acetone in Skellysolve B. Therefore, in order to locate the cryptoxanthin band approximately on a magnesia column, a mixture of extracts from yellow corn and from tomato pomace (as a source of lycopene) was passed through the column and eluted with 10% acetone in Skellysolve B. Extracts were saponified before passing through the column. The band above lycopene which was assumed to be cryptoxanthin appears to be eluted with the prescribed eluent. Without saponification the bands are not as distinct and as easily separated, but spectrophotometric readings on total eluted pigments with or without saponification are approximately the same (Table VI). Furthermore, the band assumed to be cryptoxanthin when dissolved in Skellysolve B and subjected to light absorption studies showed maxima at 485 and 452 mμ. This indicates a likelihood that cryptoxanthin is extracted and determined along with carotenes by use of the proposed procedure.

XANTHOPHYLLS

Inasmuch as lutein has been found to be a constituent of yellow corn (*12*) and is also present in alfalfa meal, the possibility of the elution of this xanthophyll along with the carotenes was investigated. According to Strain (*10*) lutein, being a dihydroxy compound, is much more strongly adsorbed on a magnesia column than is the monohydroxy polyene, cryptoxanthin. α- and β-carotenes, which do not contain the strongly polar hydroxyl group, are least strongly absorbed. This indicates that lutein should be retained by the chromatographic column, and the provitamin A pigments allowed to pass through.

The proposed solvent mixture is composed of polar liquids which should exert a considerable eluting effect if present in quantities in the solution passed through the adsorption column. However, these solvents may be removed by evaporation according to the proposed procedure, leaving only traces (less than 1 ml.).

The effect of traces of the solvent mixture was determined as follows:

Two samples of dehydrated alfalfa meal and two samples of corn gluten meal were extracted and the proposed procedure was followed through the point where the solvents are evaporated under reduced pressure. Then instead of being dissolved in 10% acetone eluting reagent, the residue was dissolved in 25 ml. of Skellysolve B. These solutions of the various samples were passed through the magnesia–Super-Cel adsorption columns. In place of being eluted with 10% acetone, which according to the procedure usually requires not over 75 ml. for complete elution of the carotene, the columns were washed with comparatively large volumes of Skellysolve B. The chromatograms developed well with very distinct bands of pigments, which would not have been the case if the traces of solvents had any pronounced effect of reducing the adsorptive power of the column. The alfalfa meal columns were eluted with 300 ml. of Skellysolve B. No pigment passed through with even this large volume of eluting reagent and the β-carotene band passed down the column less than half way. The two corn gluten meal columns were eluted with 250 ml. of Skellysolve B. The lowest band, which was identified as α-carotene, just reached the bottom of the column. The incomplete elution by use of 250 to 300 ml. of Skellysolve B containing traces of the solvents in question is compared with the complete elution by less than 100 ml. of 10% acetone.

This indicates that traces of the solvents left after evaporation do not exert an unfavorable eluting effect. Consequently, the possibility is reduced that traces of the solvents would release xanthophylls, allowing them to pass through the column with the provitamin A pigments and thus be spuriously included with the carotene in the solution taken for colorimetric reading.

The authors have demonstrated that they believe cryptoxanthin passes through the adsorption column by elution with 10% acetone in Skellysolve B and that the proposed method for the determination of carotene in corn and corn products includes this pigment. The literature indicates that lutein should follow cryptoxanthin down the column. Therefore, in order to examine the possibility of lutein's being eluted from the adsorption column using the proposed method, two samples of dehydrated alfalfa meal and two samples of corn gluten meal were extracted and chromatographed according to the procedure. The volume of 10% acetone needed for complete elution of the desired pigments was not over 75 to 100 ml. In the case of the corn gluten meal samples, the amount of additional 10% acetone required to elute the band following cryptoxanthin from the column was at least 200 ml. This pigment was collected and its solution in hexane was submitted to light absorption studies. The absorption spectrum of this pigment was similar to that of α-carotene and therefore was identified as lutein (*12*). As to the alfalfa meal samples, the volume of additional 10% acetone necessary to elute further color from the column was over 250 ml. Hence, the conclusion was reached that except for prolonged elution with 10% acetone, lutein and other xanthophylls are retained by the column.

The basis of the phasic separation method for the determination of carotene is that the polyene hydrocarbons such as α- and β-carotenes are epiphasic (petroleum ether phase), and free polyene alcohols, especially dihydroxy and trihydroxy polyenes which include many of the xanthophylls are hypophasic (aqueous 85 to 90% methanol phase). Cryptoxanthin, a monohydroxy polyene, is epiphasic if the methanol is more dilute than 95% whereas lutein (luteol), a dihydroxy polyene, is more soluble in the 90% methanol phase (*13*). Therefore, if a combination of pigments including carotene, cryptoxanthin, and lutein or other xanthophylls is saponified, taken up in petroleum ether, and shaken with portions of 90% methanol, most of the lutein and similar pigments should be removed by their solubility in the aqueous alcohol phase.

In order further to clarify the question of the presence of xanthophylls in the final carotene solutions obtained by the proposed method, two samples of dehydrated alfalfa meal and two samples of corn gluten meal were extracted and chromatographed according to the prescribed procedure. The resulting solutions were read colorimetrically to determine the quantity of pigments present. The solutions were evaporated under reduced pressure and mild heat and the residue of each was saponified and taken up in Skellysolve B, using the saponification procedure given above.

Effect of Saponification. The Skellysolve B solution in each case was shaken with at least eight 25-ml. portions of 90% aqueous methanol. These methanol extractions were discarded and the upper layer (Skellysolve B) was washed with water and passed through anhydrous sodium sulfate into a volumetric flask. Solutions were made up to volume and were used for colorimetric readings to determine quantities of carotene present. Results are shown in Table VII.

Considering the rigorous treatment and manipulations involved, the losses resulting from saponification and phasic separation are well within reason compared with those encountered in saponification alone (Table VI). Therefore, these losses do not necessarily reflect removal of extraneous pigments such as lutein which might have been present in the original solution, by the subsequent phasic separation with 90% aqueous methanol.

The above indicates a likelihood that noncarotene pigments are retained by the absorption column and therefore do not influence the final carotene measurements.

Table VII. Effect on Extracts of Saponification and Phasic Separation with 90% Methanol

	Carotene, Proposed Method	
	Without saponification	With saponification, phasic separation
	γ/g.	γ/g.
Dehydrated alfalfa meal I	164.0	156.0
Dehydrated alfalfa meal II	156.0	148.0
Corn gluten meal I	16.0	14.8
Corn gluten meal II	23.6	22.0

CONCLUSION

Extraction of pigments from dried alfalfa, corn, corn products, and mixed feeds using the mixed solvent is more complete than provided by extraction with alcoholic potassium hydroxide or with 30% acetone in Skellysolve B. This method has further advantages of efficacy and rapidity in determining the chromatographic carotene. Carotene assays on a limited number of fresh grass and silage samples indicate that the method may be useful and applicable when working with materials of this type. Information obtained thus far indicates that cryptoxanthin is eluted together with the carotenes in the chromatographic procedure outlined.

Hence the procedure tends to reflect the total concentration of all vitamin A-active pigments in a feed ingredient or mixture.

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Determination of Total Iron in Silicates and Other Nonmetallic Materials

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A method is presented for determining total iron in various refractory oxides, silicates, limestone, and fluorspar. The sample is fused in a cast silver crucible, and the iron is determined colorimetrically with *o*-phenanthroline. No separations are made. Accurate results are obtained with a variety of materials. Crucibles of platinum or platinum—3.5% rhodium are not suitable for the fusion because they retain an indefinite amount of the iron.

DURING the operation of an experimental electric arc furnace for melting various refractories, the need arose for a rapid and accurate method of determining total iron. A colorimetric method was judged to be best suited for the quantity of iron involved. Of the reagents suitable for colorimetric determination of iron, *o*-phenanthroline appeared to be the best. It is stable, colorless, and water-soluble, and is a sensitive and selective reagent for ferrous iron, which works equally well between pH 2.5 and 8.5. The color conforms to Beer's law and under some conditions is so stable that after 6 months' standing (plus 100 hours under ultraviolet radiation) there is no appreciable change in either hue or intensity (*5*).

An iron-sensitive phenanthroline, 2-methyl-(1,10)-phenanthroline, was first discovered by Gerdeissen (*6*). However, he did not mention the ferrous iron complex, which was first reported by Blau (*1*, *2*), who in 1898 synthesized *o*-phenanthroline (*3*). Application of the ferrous iron–*o*-phenanthroline complex as an oxidation-reduction indicator did not come until 1931, when it was introduced by Walden, Hammett, and Chapman (*10*). Use of *o*-phenanthroline as a reagent for ferrous iron was reported by Saywell and Cunningham in 1937 (*9*) and by Hummel and Willard in 1938 (*8*). In 1938 an exhaustive study of the reaction was made by Fortune and Mellon (*5*). Since 1938, numerous reports have appeared on further applications of *o*-phenanthroline as a redox indicator and as a reagent for ferrous iron. At present, *o*-phenanthroline is the most widely used reagent for determining small amounts of ferrous iron, or, after reduction, of total iron.

Bowen and Schairer (*4*) found that platinum crucibles removed too much iron to be usable in a phase-equilibrium study of the ferrous oxide–silica system. They stated that platinum has a marked disadvantage for this purpose. Except under strongly oxidizing conditions it reduces iron from its compounds and takes iron into solid solution; in all cases some iron was removed from the charge by the platinum crucible (*4*). The mixtures used by Bowen and Schairer were very high in total iron content and were not in contact with a large excess of flux. These conditions were different from those of the present study.

EXPERIMENTAL

Inasmuch as solution of the samples in hydrofluoric and other acids is not necessarily complete, a fusion is necessary. However, when a fusion with sodium carbonate or mixtures of sodium carbonate and sodium borate pentahydrate is made in platinum crucibles, the results for iron are totally unreliable. The platinum crucibles themselves remove part of the iron from the sample. This phenomenon works a twofold disadvantage: Assuming a clean platinum crucible to start with, iron is lost to the crucible from the first sample, and low results are obtained; and this iron is retained in the crucible and released to later samples, particularly those low in iron.

If a fusion method were to be successful, other types of crucibles had to be used. Nickel ions from nickel crucibles interfere with the colorimetric determination of ferric oxide (*5*). Porcelain or quartz crucibles are not sufficiently resistant to the melt, and alumina, titanium dioxide, and zirconium dioxide crucibles are too porous. Thick-walled silver crucibles proved to be the best of those tested.

SPECIAL EQUIPMENT

A crucible cast from 99.9+ fine silver is needed, although one could be turned on a lathe from a silver rod. Dimensions of a 40-ml. crucible are: height, 4.5 cm.; inside diameter, average, 2.8 cm. with taper; thickness of wall and bottom, 3 mm. The silver is melted in a graphite crucible and then poured into a graphite mold machined to give the above dimensions.

PROCEDURE

Grind the sample to a fineness that eliminates nonhomogeneity as a factor in the analysis. This fineness will always be at least −200-mesh and may be lower. A hard, iron-free mortar and pestle of agate, mullite, or boron carbide is recommended. For samples with 0.2 to 10% iron, take a 100.0-mg. sample; for samples with 0.00 to 0.2% iron, take a 300.0-mg. sample. With either, weigh accurately, and transfer to a thick-walled, silver crucible, which should be of about 30- to 50-ml. capacity. Add 1.0 gram of sodium carbonate and 1.0 gram of sodium borate penta- or decahydrate and mix thoroughly. Heat over a low flame until water is driven off and the flux has melted. Finish dissolution of sample by briskly heating the crucible, at the same time rotating it in the flame with a pair of tongs. When fusion is

Table I. Loss of Ferric Oxide from Sample to Clean Platinum–3.5% Rhodium Crucibles

Sample	Fe_2O_3 Present, %	Fe_2O_3 Found, %	Difference, %
Cordierite	1.2[a]	0.5	−0.7
Cordierite	6.0[a]	3.3	−2.7
Cordierite	6.0[a]	4.7	−1.3
Cordierite	6.0[a]	5.2	−0.8
Plastic clay 98[b]	2.04	1.65	−0.39
Bauxite 69[b]	5.66	4.20	−1.46

[a] Determined by standard titration procedures (*7*).
[b] Bureau of Standards sample.

Table II. Gain of Ferric Oxide into Samples from Ferric Oxide–Contaminated Platinum–3.5% Rhodium Crucibles

Sample[a]	Fe_2O_3 Present, %	Fe_2O_3 Found, %	Difference, %
Argillaceous limestone 1A	1.63	1.73	+0.10
	1.63	2.19	+0.56
Burnt refractory 77	0.90	1.25	+0.35
Flint clay 97	0.98	1.67	+0.69
Phosphate rock 56A	2.18	3.56	+1.38
Silica brick 102	0.66	1.00	+0.34

[a] Bureau of Standards samples.

complete, run the melt onto the side walls of the crucible. This practice aids solution. It is well to remember that the melting point of silver is 960.5° C.

Cool to room temperature in air or in a water bath. Dissolve directly in the crucible, by using 25 ml. of 1 to 4 hydrochloric acd (1 part of concentrated hydrochloric acid to 4 parts of water by volume) and setting the crucible on a hot plate. Do not place the crucible in a beaker for solution of sample. Flakes of silicic acid may settle out from samples high in silica, but they apparently do no harm. When solution is complete make to 100 ml. in a volumetric flask. Silver chloride, which comes from reaction of the dissolved silver and chloride, will turn the solution cloudy and must be removed. There are several ways of doing this: by centrifuging, by filtration, and by gravity settling. Silver chloride must be completely removed by one of these methods. Whatever the method, an aliquot of the clear liquid is used for analysis. If iron is 0.2% Fe_2O_3 or lower, as much as 75 ml. should be used. If iron is higher, the aliquot should be within the range of the instrument used for measuring color intensity. In either case, a transfer pipet should be used.

Transfer the sample to a 100- or 150-ml. beaker, and add 2.5 ml. of 10% hydroxylamine hydrochloride solution and 20 ml. of 0.1% *o*-phenanthroline solution (both by weight in distilled water). Using a glass electrode pH meter, adjust the pH of the solution to 2.5 to 3.0 with a sodium carbonate–free sodium hydroxide solution. Transfer to a 100-ml. volumetric flask, make to the mark, and mix. Measure color intensity with any suitable colorimetric equipment. With a Beckman spectrophotometer, the absorption was at a maximum at 512 mμ. Compare the color intensity with previously prepared standards, and calculate per cent ferric oxide.

DISCUSSION AND DATA

The most commonly used crucibles of the analytical laboratory—those of platinum and/or platinum–3.5% rhodium—could not be used for the fusion. When clean platinum–3.5% rhodium crucibles are used, the samples lose iron to the crucible, giving the low results shown in Table I. However, if platinum-rhodium crucibles, which are apparently clean, but actually are contaminated with iron, are used, the samples gain iron from the crucible, giving the high results shown in Table II. The iron contamination is evident on heating for 20 to 30 minutes at 1000° C. in an oxidizing atmosphere. These data clearly indicate that platinum-rhodium crucibles cannot be used for the fusion unless, after solution and removal of the melt, the crucibles are reheated and leached with hot acid until all iron lost to the crucible is recovered.

The analyses of nonmetallics in platinum crucibles reported in Tables I and II show that the iron compounds present in the melt are in equilibrium with metallic iron (*4*). The platinum crucible actually acts as a reservoir to take up or release iron to the melt, according to the equilibrium conditions at the particular moment. After the melt has been removed from the crucible, several heatings in an oxidizing atmosphere, with intervening leaching with hot hydrochloric acid, are usually necessary to remove completely the iron held by the platinum in solid solution. The iron is diffused to the surface of the crucible, where it is oxidized and can be removed. In the analysis of iron-bearing rocks and minerals where a sodium carbonate fusion has been made in platinum, the use of the same crucible for both the ignition of the silica and the original fusion is a necessity. Furthermore, the crucible should be heated in an oxidizing atmosphere after solution of the nonvolatile matter from the silica to ensure complete recovery of iron. Any blackening of the crucible on reheating usually indicates iron.

Table III. Direct Colorimetric Estimation of Ferric Oxide after Fusion in Silver Crucibles[a]

Electrotechnical Laboratory Samples	Fe_2O_3 Present, %	Fe_2O_3 Found[b], %
Sillimanite 2254	0.88	0.94
Electrocast alumina 2257	0.06	0.06
Mullite 2258	1.60	1.57
Electrocast refractory (corundum + mullite) 2323	1.17	1.06
Electrocast refractory (corundum + mullite) 2324	0.72	0.68
Kenya kyanite, 2637	0.34	0.36
Cordierite 1	1.20	1.20
Cordierite 1a	1.20	1.25
Cordierite 3	6.00	6.05
Ball clay 2290	0.71	0.72
Bureau of Standards samples		
Argillaceous limestone 1A	1.63	1.60
Phosphate rock 56a	2.18	2.11
Bauxite 69	5.66	5.71
Feldspar 70	0.03	0.032
Burnt refractor 77	0.90	0.92
Fluorspar 79	0.15	0.12
Dolomite 88	0.084	0.081
Opal glass 91	0.081	0.073
Plastic clay 98	2.05	2.07
Soda feldspar 99	0.067	0.073
Silica brick 102	0.66	0.68
Burned magnesite 104	7.06	6.98
Soda-lime glass 128	0.039	0.040
Crucible blank (10 samples)	....	0.007

[a] About one half of determinations are single, remainder are averages of two or more values.
[b] % Fe_2O_3 found corrected for blank.

Many types of crucibles were tried but eliminated for various reasons, such as interference with colorimetric reaction, insufficient chemical resistance, and too high porosity. Silver crucibles proved to be the best available. Gold crucibles might be satisfactory, but no data are available at this time. The results obtained with silver crucibles by using the procedure on a number of Electrotechnical Laboratory and Bureau of Standards samples are shown in Table III. The agreement between ferric oxide present and found is shown to be excellent, but results such as these are obtained only after considerable effort to obtain suitable iron-free silver crucibles. Some of the commercial thin-walled, spun-silver crucibles do not have a sufficiently low blank, even after several fusions, to be usable for the lower iron samples. The thin-walled-type crucibles are easy to overheat in spots, with resultant holes, and to crack at strains that might have been formed during the spinning process used in making them. With the cast crucibles, a thickness of 3 mm. was enough to give such uniform heating that after 50 fusions the crucibles were in excellent condition, with no evidence of cracking or melting. Some of the crucibles had high initial blanks which may have been caused by a slight contamination with iron from the graphite crucible and mold. A crucible and mold other than graphite, such as refractory oxides, might be more satisfactory. However, after four fusions to clean the crucible, the blank remained constant at 0.007 (±0.001) % ferric oxide.

Because some of the samples contained only 0.09 mg. of ferric oxide, precautions had to be taken to prevent contamination of the sample. Dust was carefully avoided. To prevent contamination of the crucible with other metals, the crucibles were held with silver-wrapped Nichrome tongs and set on a silver sheet. Solution of the fusion was always accomplished by pouring the acid into the crucible—in no case was the crucible set in a beaker. Once the crucible was clean, these precautions helped to produce a low and constant blank.

The silver must be removed from the solution before addition of the *o*-phenanthroline, because a chemical reaction takes place which produces a precipitate. Therefore, no advantage would be obtained by the use of any acid other than hydrochloric acid to dissolve the melt without precipitating any silver salts. Of the methods for removing silver chloride, centrifuging is the easiest and fastest; a clear supernatant liquid is obtained in a few minutes. Centrifuging was the method largely used in this study. After coagulation, the precipitate was easily removed by filtration. If sufficient time were allowed, the precipitate settled by gravity alone.

With samples high in silica, such as feldspar or silica brick, a precipitate of silicic acid was obtained, but it apparently did not interfere in any way. It was removed along with the silver chloride. Buffers of ammonium acetate are used frequently in iron determinations to produce the correct pH, but these reagents cannot be used under the conditions described. The ammonium acetate would produce a heavy gel of silicic acid that would interfere seriously. The pH of the solution must be adjusted with a glass-electrode pH meter, or by other means that introduce no extraneous color or interfering ion.

Accurate results were obtained with a wide variety of samples, including various silicates, phosphates, and fluorspar. The number of ions interfering with the determination, and the extent of their interference, are low (*5*). Among ions that might interfere somewhat are nickel, bismuth, molybdate, tungstate, and cyanide. If present at all, the percentage of these ions would be very low in the materials for which this procedure was tried and for which it is recommended. However, any change in hue or any precipitation should serve as a warning for further study of the material. Silicon carbide, which is apparently not wetted very well by the molten flux, could not be completely decomposed at the temperature used.

Single determinations have been made in 15 minutes when all apparatus was ready and when the removal of silver chloride caused no difficulty. The method is easily applied concurrently to a large number of samples.

CONCLUSION

Platinum-rhodium crucibles cannot be used for the precise estimation of iron after a sodium carbonate-borate fusion unless the iron lost to the crucible is recovered by repeated heating and leaching with hot acid. However, excellent results without loss of iron are obtained with a wide variety of materials when the fusions are made in thick-walled cast silver crucibles.

ACKNOWLEDGMENT

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Photometric Determination of Molybdenum by Acetone Reduction of the Thiocyanate

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A photometric method for the determination of small amounts of molybdenum in solutions is presented. As in previous methods, molybdenum is determined by the yellow-amber color of its thiocyanate. The use of acetone as a reducing agent increases the sensitivity and eliminates the rapid fading of the color complex encountered when other reducing agents are used.

The yellow-amber color developed by molybdenum, a thiocyanate salt, and a reducing agent has been used for a number of years for the colorimetric determination of small amounts of molybdenum. Stannous chloride has been the most common reducing agent used. Hurd and Allen (*2*) made a study of solvent extracting solutions, concentrations of reagents, and other variables involved, and determined the conditions which allowed the maximum color development and minimized the rate of fading of the color complex. Grimaldi and Wells (*1*) dispensed with solvent extracting solutions and developed the color in a water-acetone solution using stannous chloride as a reducing agent. This method stabilized the color somewhat.

In trying to determine the amounts of molybdenum in soils, the above methods were used by the authors and attempts were made to evaluate the color with an Evelyn photometer. Rapid color fading was found to occur with each method. Although it was possible to standardize the procedure somewhat by establishing a fixed period of time before the readings were taken, it was thought highly desirable to find a reducing agent that would give color stability over a long period of time. It was felt that color stability would certainly improve the accuracy and convenience of the determination. Therefore, a method was developed in which acetone is used directly as a reducing agent and by which color stability is obtained for a period of 48 hours. The sensitivity of the determination is also increased over the two previous methods.

REAGENTS

Potassium thiocyanate (water solution). Dissolve 10 grams of potassium thiocyanate in 100 ml. of distilled water.

Table I. Transmittancies Obtained with Different Concentrations of Molybdenum and Various Reducing Agents

Reducing Agent	Molybdenum Concentration, Parts per Million			
	1	5	10	20
	%	%	%	%
Acetone	69.5	20.5	7.0	1.0
Stannous chloride	78.0	35.0	19.0	8.0
Camphor	99.0	73.0	71.0	58.0
$NaHSO_3$	88.0	..	..	76.0
$NaHSO_3$ + Metol	76.8	71.0	68.3	56.0
1 Amino-2-naphthol-4-sulfonic acid + Na_2SO_3 + $Na_2S_2O_5$	72.5	71.0	68.5	67.3
Hydroxylamine hydrochloride	97.0	97.0	92.0	88.0

Acetone, reagent grade.

Hydrochloric acid, specific gravity 1.18 to 1.19.

Standard molybdenum solution for preparing calibration curve (1000 p.p.m. of molybdenum). Prepare a stock solution containing 1000 p.p.m. of molybdenum by dissolving 1.8401 grams of dry ammonium molybdate·[$(NH_4)_6Mo_7O_{24}.4H_2O$] in water and diluting to 1 liter. Prepare working standards by quantitative dilution of the stock solution.

PROCEDURE

Evaporate or dilute the molybdenum solution to be analyzed until 20 ml. of the solution contain from 5 to 1000 micrograms of molybdenum. Place 20 ml. of the solution in a 50-ml. volumetric flask and add enough hydrochloric acid or other nonoxidizing acid to make the final 50 ml. of solution 1.2 to 2 *N* in respect to acid. When using water solutions of molybdenum, 7 ml. of hydrochloric acid are sufficient. Add 3 ml. of 10% potassium thiocyanate solution and 15 ml. of acetone, and place the sample in a water bath at 60° to 70° C. for at least 20 minutes. When the molybdenum concentration of the solution is in the range given above, loss of acetone during heating is not of any importance even when the heating continues as long as 2 or 3 hours. Cool, dilute to volume, and determine transmittancy in a filter photometer or spectrophotometer at 420 mμ. Determine parts per million of molybdenum in the solution by reference to a standard calibration curve prepared from known standard molybdenum concentrations.

If it is present in high concentrations, ferric iron interferes with the molybdenum determination. If ferric iron is left in solution, a fine precipitate is formed when the reduction process is carried out. If its concentration in the final solution exceeds 100 p.p.m., the iron should be removed from the solution by standard quantitative procedures before reduction. Precipitation by raising the pH of the solution with ammonium hydroxide was found to be a satisfactory method for removing the iron. If the iron concentration is less than 100 p.p.m., the determination can be carried out without its removal by extending the period of heating during reduction to approximately 1 hour. However, because a longer period of heating is required, it is recommended that the removal of iron be made a standard procedure for all determinations. The iron should be removed from the solution before the acid, thiocyanate, and acetone are added.

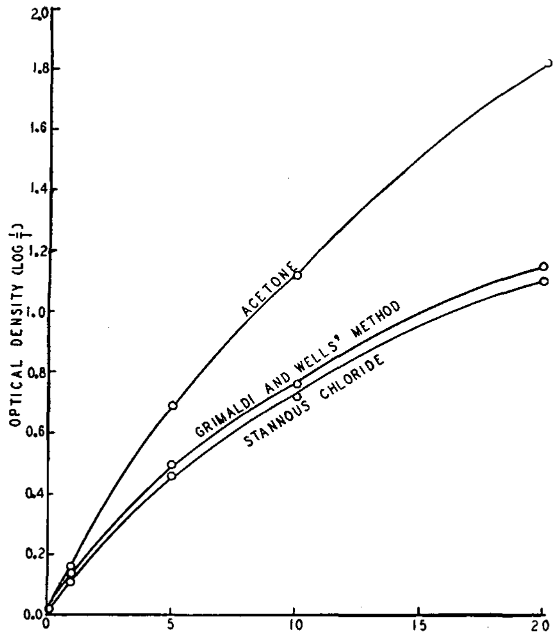

Figure 1. Intensity of Molybdenum Color Complex Developed by Different Reducing Agents

Inasmuch as the molybdenum concentration of solutions may often be increased by evaporation and acetone reduction provides a highly sensitive method of determination, it is not recommended that the colored complex be extracted with ether or other solvents unless it is impossible to evaporate the solution sufficiently.

DISCUSSION AND RESULTS

Table I compares the light transmittancies obtained with different molybdenum concentrations using various reducing agents. All the reducing agents were tried at several concentrations. Sodium bisulfite, sodium bisulfite and Metol, hydroxylamine hydrochloride, 1 amino-2-naphthol-4-sulfonic acid plus sodium sulfite plus sodium persulfate, and camphor gave color stability but failed to give sufficient sensitivity for the determination of small amounts of molybdenum. Acetone was the only reducing agent tested that gave both color stability and sensitivity.

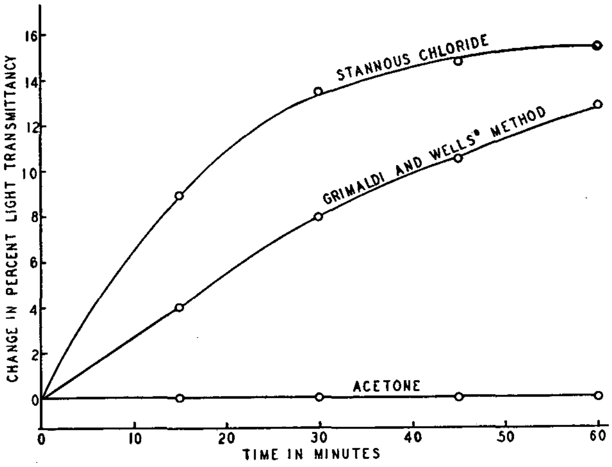

Figure 2. Rate of Fading of Molybdenum Color Complex with Different Reduction Methods

Solutions contain 5 p.p.m. molybdenum

A comparison of the intensity of the color complex developed by different reducing agents is shown in Figure 1, where optical density is plotted against parts per million of molybdenum. The acetone reduction method increases the intensity of the color complex, thus allowing a more precise determination of small amounts of molybdenum—2 p.p.m. molybdenum, for example, produced an optical density of 0.20 using stannous chloride, 0.23 using the Grimaldi-Wells method, and 0.32 using acetone. The increase in color intensity is even greater at the higher concentrations of molybdenum.

A comparison of the rate of fading of the color complex using the three reduction methods is shown in Figure 2, where changes in transmittancy are plotted against time in minutes. All comparisons were made using 5 p.p.m. of molybdenum. Although a significant amount of fading occurred in 5 minutes and the color intensity was greatly diminished in 1 hour when stannous chloride was used as the reducing agent, acetone reduction produced an unchanging color. The fading of the color complex using stannous chloride is more rapid at higher concentrations; however,

Table II. Effect of Time of Heating at 70° C. on Development of Color Complex in Solutions Containing 5 P.P.M. of Molybdenum

Time of Heating, Minutes	Light Transmittancy, %
10	20.5
20	20.5
30	20.3
40	20.3
50	20.5
60	20.3

rapid fading is still encountered at concentrations of 1 p.p.m. of molybdenum. The acetone reduction method has given color stability at concentrations up to 20 p.p.m. of molybdenum for a period of 48 hours.

As in previous methods, the acidity of the solution in which the molybdenum determination is carried out must be carefully controlled when acetone is used as the reducing agent. It was found that the final solution should be between 1.2 and 2 *N* in respect to hydrochloric acid or other nonoxidizing acids in order to obtain accurate results. This is essentially the same as determined by Hurd and Allen (*2*) using stannous chloride.

Iron is the only interfering element that has been encountered by the authors in their experimental work. However, it is assumed that elements interfering with the determination of molybdenum as the thiocyanate by other reducing methods will also interfere with the acetone reduction. Grimaldi and Wells (*1*) have devised a method for eliminating the interference of tungsten and vanadium. They have also found that phosphates interfere with the color reaction when tungsten is present in appreciable amounts and that large amounts of nitrates cause excessive color fading.

Table II compares transmittancy values obtained after various periods of heating during the reduction process. An examination of the table seems to indicate that heating for 10 minutes is sufficient for color development. It is recommended that heating be continued for 20 minutes to ensure full color development. This allows for the reduction of small amounts of ferric iron, and also allows for a range of temperatures from 60° to 70° C. during the period of heating.

The temperature of the solutions at the time of reading may vary from 15° to 40° C. without affecting the transmittancy values. Considerable variations in room temperature are, therefore, allowable.

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Estimation of Solubility of Solids in Liquid Ammonia and Liquid Sulfur Dioxide

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A convenient and rapid method for the estimation of the solubility of solids in liquefied gases is described, and data thereby obtained are compared with earlier results obtained by other methods. Solubility data at 25° C. for sodium chloride and rubidium chloride in liquid ammonia, and sodium iodide, potassium bromide, and twelve alkaline earth halides in liquid sulfur dioxide are given.

CONSIDERABLE effort has been expended in the development of methods for the determination of the solubility of solids in liquefied gases in general and liquid ammonia in particular (*1*, *3–5*, *8–12*). All the methods thus far employed are characterized by more or less elaborate equipment and involved manipulative procedures designed to provide highly accurate results.

In connection with certain work in progress in these laboratories there has arisen the need for a simple and rapid method for the estimation of the solubility of a wide variety of solid compounds in solvents such as liquid ammonia and liquid sulfur dioxide. For these purposes it is usually sufficient to know the relative order of magnitude of the solubilities. Accordingly, attention has been directed toward the development of a method characterized by its simplicity and rapidity of application.

EXPERIMENTAL

Materials. Commercial liquid ammonia was dried and dispensed as described by Johnson and Fernelius (*7*). Sulfur dioxide from a commercial cylinder was dried by passing the gas through concentrated sulfuric acid, then through phosphorus pentoxide. The gas was condensed in a trap cooled with dry ice and acetone, and subsequently distilled into the tubes used in the solubility determinations.

All solids used in solubility determinations were prepared and/or purified, dried, and analyzed (*11*) before use.

Procedure. A weighed sample of the solid (approximately 0.1 gram) is introduced into one end of a glass filter tube about 18 cm. in length, with an inside diameter of 5 to 10 mm., and with a fritted-glass disk (porosity C or D, *2*) at the mid-point. This end of the tube is sealed and cooled, and the tube and its contents are weighed. The tube is flushed out with the anhydrous gas, after which the open end of the tube is attached to the source of anhydrous gas. The end of the tube containing the solid is immersed in a dry ice–acetone bath at a temperature of approximately −75° C. and a suitable quantity of solvent (0.8 to 1.0 gram) is condensed on the solid sample. The open end of the tube is then sealed off under conditions that permit determination of the weight of the glass removed in making the seal. (This is done by use of a weighed glass rod, determination of the weight of rod plus glass removed, and getting the weight of the latter by difference. The net weight loss involved in this procedure has been found not to exceed 0.8 mg. and is usually of the order of 0.4 mg.)

The sealed tube is allowed to warm to room temperature, weighed, and agitated in a thermostat (25.0° ± 0.1°) for 48 hours. The tube is removed from the thermostat, inverted, and centrifuged at 2000 r.p.m. for from 3 to 5 minutes, thus effecting a separation of the saturated solution and the excess undissolved solid. The end containing the saturated solution is cooled to

−75°, and the other end is drawn out to a fine capillary through which the solvent is allowed to escape. Thereafter, the tube is evacuated at about 10^{-3} mm. of mercury for from 1 to 2 hours.

This procedure permits one to determine the weight of solute in the saturated solution by (1) chemical analysis, (2) removal of that portion of the tube which contains the sample of the solid that was dissolved, and determination of its weight before and after removal of the solid, or (3) the similar determination of the weight of excess solid, and the weight of the dissolved portion by difference. All three methods have been employed; although they lead to substantially the same results, the second is preferred from the standpoint of rapidity and simplicity. The first method must be used if it is desired to establish the composition of solvates or the absence of solvolytic reactions.

The weight of solvent may be measured by (1) determination of the weight of the tube assembly before and after introduction of the solvent and application of the correction for the weight of glass removed, (2) determination of the weight of the tube assembly before and after evaporation of the solvent, or (3) collection and subsequent determination of the solvent volatilized—e.g., collection of ammonia in standard hydrochloric acid, followed by titration of excess acid. Methods 1 and 2 gave results that were in consistently good agreement, whereas method 3 proved to be the most time-consuming and the least reliable; method 1 is preferred.

Solubility of Sodium Chloride in Liquid Ammonia. Data from six independent determinations of the solubility of sodium chloride led to a value of 4.2 ± 0.2 grams of sodium chloride per 100 grams of ammonia.

Solubility of Rubidium Chloride in Liquid Ammonia. Four measurements gave a value of 0.22 ± 0.03 gram of rubidium chloride per 100 grams of ammonia.

Solubility of Sodium Iodide in Liquid Sulfur Dioxide. The solubility was found to be 2.1 ± 0.2 grams of sodium iodide per 100 grams of sulfur dioxide (six measurements).

Solubility of Potassium Bromide in Liquid Sulfur Dioxide. Five determinations gave a value of 0.38 ± 0.05 gram of potassium bromide per 100 grams of sulfur dioxide.

Table I. Solubility of Alkaline Earth Halides in Liquid Sulfur Dioxide at 25° C.

Salt	Solubility, G. Salt/100 G. SO_2	Salt	Solubility, G. Salt/100 G. SO_2
CaF_2	0.08 ± 0.01	$SrBr_2$	0.02 ± 0.01
$CaCl_2$	0.02 ± 0.01	SrI_2[b]	0.49 ± 0.01
$CaBr_2$	0.02 ± 0.01	BaF_2[b]	0.02 ± 0.01
CaI_2[a]	1.8 ± 0.2	$BaCl_2$	0.03 ± 0.01
SrF_2	0.02 ± 0.01	$BaBr_2$	<0.01
$SrCl_2$	<0.01	BaI_2	0.10 ± 0.01

[a] Monohydrate.
[b] Hemihydrate.

Solubility of Alkaline Earth Halides in Liquid Sulfur Dioxide. Data relative to the solubility of twelve salts are listed in Table I. Each value is the average of either three or four independent measurements.

DISCUSSION

Sodium chloride was used as the basis for evaluation of the method described in this paper because of the availability of data for comparison. The result—4.2 grams of sodium chloride per 100 grams of solvent at 25°—is in good agreement with the value of 4.413 at 24.9° reported by Patscheke (*10*), but is somewhat higher than Hunt's (*4*) value of 3.02 grams of sodium chloride per 100 grams of ammonia at 25°. However, Linhard and Stephan (*9*) have shown that Hunt's result is probably low. In the absence of information concerning the temperature coefficient of solubility of rubidium chloride, it appears that the value of 0.22 gram of rubidium chloride per 100 grams of ammonia is in reasonably good agreement with Linhard and Stephan's (*9*) value of 0.289 gram per 100 grams of solution at 0°.

There are available for comparison only very few data on the solubility of salts in liquid sulfur dioxide and some of these have been presented only as estimates. Shatenshtein and Viktorov (*13*) reported the solubility of sodium iodide to be 1.59 grams of sodium iodide per 100 grams of sulfur dioxide at 25° and this is to be compared with the value of 2.1 grams reported here. Similarly, the value of 0.38 gram of potassium bromide per 100 grams of sulfur dioxide is comparable to their value of 0.55. Jander and Ruppolt (*6*) reported solubility data for these two salts at 0°, but the values are much higher owing to extensive solvation at the lower temperature.

Solubility data on the alkaline earth halides at 25° have been reported by others in only three cases. The value of 0.08 gram of calcium fluoride per 100 grams of sulfur dioxide falls within the range of 0.01 to 0.1 reported by Shatenshtein and Viktorov (*13*). On the other hand, the present values of 1.8 and 0.49 for calcium iodide and strontium iodide, respectively, are significantly higher than Shatenshtein and Viktorov's corresponding values of 0.75 and 0.14. These discrepancies, however, may be due to the fact that the lower hydrates of these salts were used in the present work. The relative insolubility of barium chloride at 25° is consistent with earlier reports (*5*, *6*) that this salt is insoluble at 0° and 25°.

Except in the case of the alkaline earth iodides, which are much more soluble in sulfur dioxide than are the other alkaline earth halides, the present method does not provide solubility values sufficiently accurate to permit correlation with ionic radii. The solubility of the iodides decreases with increase in cationic radius in a manner to be anticipated in view of the polarization effects attributable to the iodide ion.

This method does not provide for the establishment of the composition of the solid phase in equilibrium with the saturated solution. It does, however, permit the identification of solvates stable at 25° and 10^{-3} mm. of mercury. Among the alkaline earth halides, the solid phase was white and the saturated solution was colorless in all cases except the iodides; these gave orange colored solid phases and dark red solutions. Upon evaporation of the solvent and during removal of residual solvent by evacuation, the colors became progressively less intense. Solvates identified by determining (by analysis, *11*) the retention of solvent by known weights of the undissolved portion of the solid salts include: $CaI_2.3SO_2$, $SrI_2.2SO_2$, $BaI_2.SO_2$, and $BaI_2.3SO_2$. Less conclusive data suggested the existence of the solvates: $(SrCl_2)_3.SO_2$ and $BaCl_2.SO_2$. The existence of the solvates $CaI_2.4SO_2$, $SrI_2.4$ and $2SO_2$, and $BaI_2.4$ and $2SO_2$ has been reported by Jander and Ruppolt (*6*).

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Coulometric Titrations with Iodine

Titration of Arsenic and Use of an Amperometric End Point

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The conditions under which electrolytically generated iodine can be used for secondary coulometric titrations and the end point determined by an amperometric method have been investigated. Tripositive arsenic in quantities from 64 to 1200 micrograms has been titrated in solutions having a pH value of 8 with an average error without regard to sign of 0.6 microgram.

THE advantages of the secondary type of coulometric process, in which an intermediate half-cell reaction is caused to take place at the electrode, have been discussed by Szebelledy and Somogyi (*7*) and by Meier, Myers, and Swift (*4*). A number of studies have been made of the use of bromine as an intermediate oxidizing agent for the titration of reducing agents such as hydrazine (*9*), hydroxylamine (*10*), thiocyanate (*8*), thiodiglycol (*6*), tripositive arsenic (*5*), tripositive antimony (*1*), and iodide (*11*). The use of cuprous copper as an intermediate reducing agent for the titration of chromate and vanadate has also been investigated (*4*).

In order to extend the application of such processes, especially to selective titrations, it seemed desirable to investigate the application of other intermediate half-cell reactions having various standard potentials and capable of being used in solutions over an extended range of pH values.

The criteria establishing the suitability of any proposed intermediate half-cell reaction are the following: The active state of this intermediate must be capable of being produced electrolytically with 100% current efficiency. The state thus produced must then be capable of rapidly and stoichiometrically reacting with the agent to be titrated. Lastly, there must be a method of determining an end point, and if the amperometric method is chosen, an excess of the active state of the intermediate must cause a current between the two indicator electrodes which for the required concentrations and conditions is directly proportional to the concentration of that state.

An investigation of the iodide-iodine half-cell as such an intermediate has been made and the pH range has been established under which the titration of tripositive arsenic can be made with iodine and the excess iodine determined amperometrically.

EXPERIMENTAL

Chemicals. Standard solutions of tripositive arsenic were prepared in the following way: A 1-gram sample of Bureau of Standards arsenious oxide which had been dried for 2 hours at 120° C. was accurately weighed out and dissolved in 20 ml. of water containing 2 grams of sodium hydroxide. The resulting solution was acidified by adding 10 ml. of 3 volume formal (*VF*) sulfuric acid and was diluted to approximately 100 ml. The weight of the resulting solution was determined. Solutions prepared in this way were used as stock solutions, none of which was kept for more than 4 weeks. Weighed samples of these stock solutions were diluted to appropriate volumes to provide the standard solutions, and none of these was kept for more than 2 days.

Solutions of 1 *VF* potassium iodide were prepared by dissolving weighed samples of the solid in 0.005 *VF* sodium carbonate.

A solution buffered to pH 8 was prepared by dissolving solid sodium hydroxide in a solution 0.25 *VF* in sodium dihydrogen phosphate until the correct pH was obtained as measured with a Beckman pH meter.

Other buffered solutions were prepared in the following way: The weight of a salt corresponding to one of the ionic species used in the buffer solution sufficient to give a solution at least 0.2 *VF* in that salt was dissolved in water. The corresponding acid or sodium hydroxide was added until the desired pH was obtained. Limited range pHydrion indicator paper was used instead of the pH meter for determining pH values greater than 10.

In all the above solutions, reagent grade chemicals were used.

The laboratory distilled water was often found to contain small amounts of an unknown oxidizing agent. This oxidizing agent was removed by boiling the distilled water for about 20 minutes, and then bubbling nitrogen through it for about 30 minutes. Only water treated in this way was used.

Apparatus. The apparatus was essentially the same as that described by Meier, Myers, and Swift (*4*), with the following changes: In place of the laboratory direct current supply, the voltage of which was found to vary slightly, use was made of a simple voltage-regulated rectifier which was connected to the alternating current line through a voltage-regulating Sola transformer. The generating cathode was enclosed in a shield rather than the anode. Finally, except where noted, nitrogen gas, after being passed successively through 6 *VF* sodium hydroxide and soda lime, was maintained above the solutions being titrated.

Preliminary Adjustment. The current of the generation circuit was determined by measuring the voltage drop across a standardized 199.87-ohm resistance through which the generation current was passing. At the low rate of generation, this current was found to correspond to the oxidation of 1.0385×10^{-8} equivalent per second, while the high rate current corresponded to 1.0393×10^{-7} equivalent per second.

The indicator potential was measured with a Gray Instrument Company Queen potentiometer.

One volume formal sulfuric acid was placed in the cathode shield.

Before each set of titrations the indicator electrodes were shorted to the generator anode, a potassium iodide solution was placed in a titration cell (a 40 × 80 mm. weighing bottle), and iodine was generated in the solution for 100 seconds at the high rate.

Titration Procedure. The initial step in carrying out a set of titrations was the determination of the blank time. In order to do this, a number of blanks were run. For each blank, 5 ml. of 1 *VF* potassium iodide, 20 ml. of the buffer of pH 8, and 25 ml. of water were placed in a titration cell. The indicator potential was adjusted to an initial value of 0.15 volt. The generation current, passing through a dummy resistance, was then adjusted to the desired value. Finally, iodine was generated for short intervals of time depending upon the rate of generation used (0.5 second for the high rate, 2.5 for the low). Twenty seconds were allowed after each interval of generation for equilibrium conditions to be approached, and the indicator current and the generation time were recorded. A plot of indicator current *vs.* time of generation was made, and the linear portion of this plot, from approximately 10 to 40 μa., was extrapolated to zero indicator current. The average value of the generation time intercepts for a group of blanks was designated as the blank time.

To maintain the sensitivity of the indicator electrodes, they were shorted to the generator anode, and iodine was generated for 50 seconds at the high rate after each blank and every titration. Then the solution was removed from the apparatus, and the electrodes were rinsed with water.

After the blank time had been determined, a group of titrations was made. Twenty-five milliliters of a standard arsenic solution were pipetted into a titration cell. To this were added 20 ml. of the buffer of pH 8 and 5 ml. of 1 *VF* potassium iodide, and the cell was rapidly attached to the apparatus. The generation current was adjusted, and titration was begun. Occasionally during titrations, small adjustments had to be made on this current.

When the indicator current began to rise, the titration was stopped, and a plot of indicator current *vs.* time of generation was constructed from data obtained in exactly the same manner as in the case of the blanks. The linear portion of this plot was also extrapolated to zero indicator current, and the generation time intercept was designated as the titration time. The blank time was subtracted from the titration time to give the corrected titration time. The corresponding weight of arsenic was calculated from the values of the corrected titration time and the rate of generation.

DISCUSSION

Potential Difference between Indicator Electrodes. In order to minimize effects due to changes in the internal and external resistance of the indicator circuit, it is desirable to choose an indicator potential which is within the range wherein the curve of indicator current *vs.* indicator potential is flattest, and which is as high as practicable within that range. This initial potential value was determined in the following way: Iodine was generated in a blank solution until an indicator current of 20 μa. was obtained when the potential difference between the indicator electrodes was 191 mv. Then this potential difference was varied, and both it and the indicator current were recorded. The data thus obtained were plotted, and the resulting graph is shown in Figure 1. This graph is essentially in agreement with similar ones obtained by Brunner (*2*). Because the flattest portion of the curve lies between 100 and 160 mv., an indicator potential of 150 mv. was chosen and was used for all subsequent work.

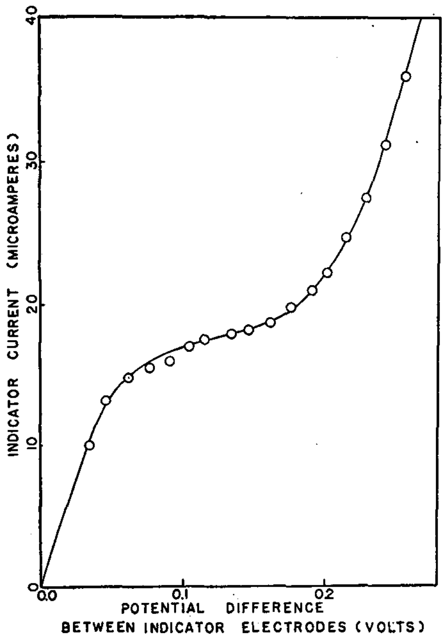

Figure 1. Variation of Indicator Current with Potential Difference between Indicator Electrodes

Iodine concentration 2 × 10^{-4} *VF*

Effect of pH on Indicator Current. In order to determine the effect of pH on the magnitude and constancy of the indicator current, blanks were run in solutions of various pH values in the manner described above, and plots of indicator current *vs.* generation time were constructed.

In all these blanks, a potential difference of 0.15 volt was used, the total volume of the solution was 50 ml., and the solutions were 0.10 *VF* in potassium iodide. The desired pH value was obtained by taking 45 ml. of either 0.5 *VF* sulfuric acid, 0.10 *VF* sodium hydroxide, 1.0 *VF* sodium hydroxide, or one of the following buffer solutions: pH 2, sulfate-monohydrogen sulfate; pH 3, dihydrogen phosphate-phosphoric acid; pH 5, acetate-acetic acid; pH 7, monohydrogen carbonate-carbonic acid; pH 8, monohydrogen phosphate-dihydrogen phosphate; pH 9 and pH 10, dihydrogen borate-boric acid; pH 11, carbonate-monohydrogen carbonate; pH 12, phosphate-monohydrogen phosphate.

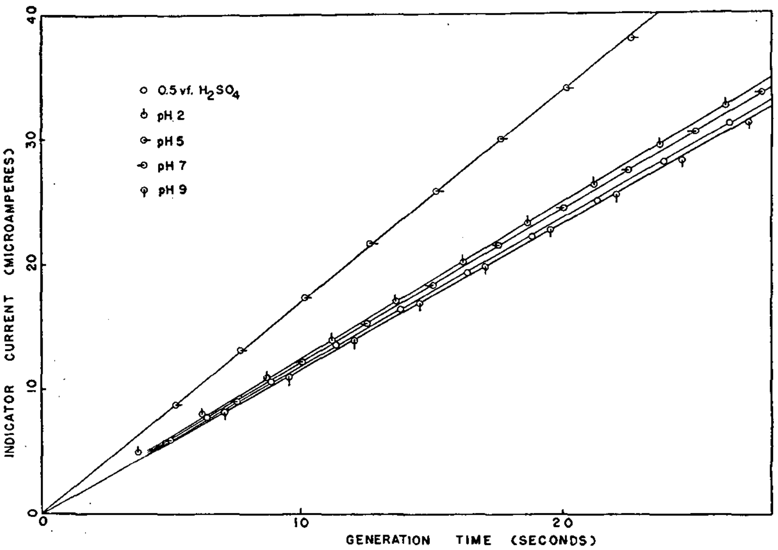

Figure 2. Indicator Current *vs.* Time of Generation at Various Hydrogen Ion Concentrations

Figure 2 shows typical data obtained at pH 9 or less. The plots have been corrected for the presence of oxidizing or reducing agents in the reagents used in preparing the buffers, by extrapolating the linear portions of these curves to zero indicator current, and by calling the intercept on the generation time axis zero generation time.

That the curves are linear over this range of pH values is evident, and the current readings were stable to ±0.2 microampere for at least 3 minutes. No conclusions can be drawn from the slopes of these curves because the sensitivity of the indicator electrodes varied sufficiently over a period of a few days to account for the different slopes shown.

Table I. Rate of Decrease of Indicator Current

pH	Indicator Current, μa.	Rate of Decrease, μa./Sec.
10	40	0.020
	25	0.014
11	48	0.07
	37	0.036
12	45	0.09
	40	0.07

In solutions having pH values of from 10 to 12 the indicator current was not stable, and its rate of decrease could be determined. At given values of pH and current these rate measurements agreed to an accuracy of ±15%, and a series of such measurements is shown in Table I. When indicator current readings were made with only 10 seconds being allowed after each period of generation for stabilization of the current, the curves of indicator current *vs.* generation time were found to be linear. Indeed, at all pH values of less than 12 only between 1 and 5 seconds were required after each period of generation for the indicator current to reach a value within 0.2 microampere of the value taken. In solutions in which the concentration of sodium hydroxide was greater than or equal to 0.10 *VF*, the rate of decrease of the indicator current was so high that no valid determination of a linear dependence could be made—for example, in 1.0 *VF* sodium hydroxide solution, the rate of decrease of this current was 0.25 microampere per second.

It is reasonable to assume that these decreases of indicator current with time at pH values of 10 or greater are due to decreases in the total iodine—i.e., zero oxidation state iodine—concentration, in view of the fact that the indicator current is linearly proportional to this total iodine concentration. Three mechanisms are possible by which this might occur: Iodine vapor may be volatilized from the solution; iodine may hydrolyze, forming iodide and hypoiodite or iodate ions; and iodine may be oxidized to iodate by atmospheric oxygen, as postulated by McAlpine (*3*). The first of these mechanisms cannot be the rate-determining one, because no comparable rate of decrease of indicator current was observed at higher hydrogen ion concentrations. The conclusion of McAlpine that air oxidation of the iodine is responsible for its disappearance in solutions of low hydrogen ion concentrations cannot be accepted because it was found that in a solution buffered at a pH of 12 the rate of decrease of the indicator current was the same within ±5% when an atmosphere of oxygen was maintained above the stirred solution as when an atmosphere of nitrogen was so maintained. Therefore hydrolysis is apparently responsible for the removal of iodine from solutions having pH values of 10 or greater.

The above observations show that the amperometric method for the determination of excess iodine may be used in solutions in which the hydrogen ion concentration is greater than or equal to 10^{-9} mole per liter and with but little difficulty may be extended to include solutions in which it is equal to 10^{-10} mole per liter. The reproducibility with which the rate of decrease of the indicator current could be observed suggests that this amperometric procedure could be used to study the rate of hydrolysis of iodine at very low concentrations.

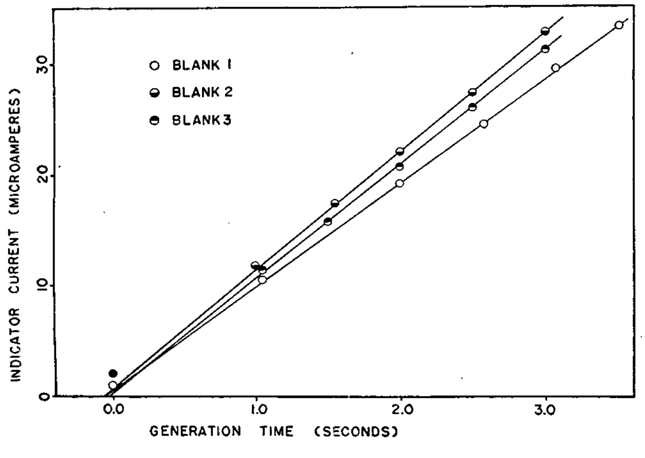

Figure 3. Indicator Current *vs.* Generation Time for a Group of Blanks

Effect of Iodide Concentration on Indicator Current. In order to determine whether any significant effect was caused by increasing the iodide concentration above the usual value, the following experiment was carried out: In a blank solution, enough iodine was generated to give an indicator current of 25 μa. Eight grams of solid potassium iodide were dissolved in the solution and the indicator current was again noted. The indicator current was found to increase 1 or 2 μa. Thus changes in iodide concentration above 0.1 *VF* have only a small effect upon the indicator current.

Accuracy of Determination of Iodine Concentrations. Figure 3 shows the curves obtained by running three successive blanks in solutions buffered to a pH of 8 and with an indicator potential of 0.150 volt, and then plotting indicator current against generation time. Though the slopes of the three lines shown differ noticeably from one another, it was found that if more blanks were run, the slopes of successive blanks would tend to become equal. When a sufficient number of blanks, on the order of three or four, had been run, total concentrations of iodine between 2×10^{-6} and 1×10^{-5} equivalent per liter could be determined to an accuracy of ±1%. However, the slopes of the curves shown have only a second-order effect on the blank time, so that for the purposes of this titration only three or at most four blanks were run to determine each blank time.

Table II. Confirmatory Titrations

Number[a]	Arsenic, Micrograms Taken	 Found	 Error	% Error
I[b] 1	69.4_3	69.3_1	−0.12	−0.17
2		69.4_7	0.05	0.07
3		69.3_5	−0.08	−0.12
	Av.	69.3_8	−0.05	−0.07
I 1	618.0	$618._6$	0.6	0.10
2		$618._9$	0.9	0.15
3		$618._6$	0.6	0.10
4		$619._3$	1.3	0.24
	Av.	$618._9$	0.9	0.15
I 1	$605._7$	$606._8$	1.1	0.19
2		$606._8$	1.1	0.19
3		$607._2$	1.5	0.26
4		$606._8$	1.1	0.19
5		$607._2$	1.5	0.26
	Av.	$607._0$	1.3	0.22
II 1	203.8	$203._9$	0.1	0.05
2		$203._7$	−0.1	−0.05
3		$203._7$	−0.1	−0.05
4		$203._7$	−0.1	−0.05
5		$203._9$	0.1	0.05
	Av.	$203._8$	0.0	0.00
III 1	$1253._1$	$1253._9$	0.8	0.06
2		$1254._0$	0.9	0.07
3		$1253._6$	0.5	0.04
4		$1253._4$	0.3	0.02
5		$1253._6$	0.5	0.04
	Av.	$1253._7$	0.6	0.05
III[c] 1	$1253._1$	$1253._5$	0.4	0.03
2		$1252._8$	−0.3	−0.02
3		$1253._5$	0.4	0.03
4		$1252._7$	−0.4	−0.03
	Av.	$1253._1$	0.0	0.00

[a] Roman numerals indicate stock solutions used.

[b] Low rate of generation used for this group only; high rate used for all other groups here represented.

[c] In this group only, no atmosphere of nitrogen above solution undergoing titration.

Effect of pH on Coulometric Titration. The upper limit of the hydrogen ion concentration range at which arsenic may be coulometrically titrated using iodine as the intermediate is determined by the rate of the reaction between iodine and arsenious acid. At a pH value of 7, this rate was found to be sufficiently high for titrations at the low rate of iodine generation. However, the high rate of iodine generation could not be used at this pH value because excess iodine accumulated in the solution before the equivalence point, causing a premature rise in the indicator current. At a hydrogen ion concentration of 10^{-5} mole per liter neither rate of generation could be used.

In order to investigate the possibility of carrying out the selective titration of other reducing agents in the presence of tripositive arsenic, experiments were made in which it was found that in solutions 0.1 *VF* in perchloric acid as much as 1100 micrograms of tripositive arsenic had no effect on the blank time or on the indicator current–generation time curve. At a pH of 3 the iodine reacted with the tripositive arsenic slowly, but at such a rate that a stable indicator current could not be obtained.

The lower limit of hydrogen ion concentration is determined by the effect of the rate of hydrolysis of iodine on the determination of the end point; this effect has been discussed above.

Confirmatory Titrations. Table II shows the data obtained from confirmatory titrations which were carried out as described above. It is seen that the titration is accurate to approximately ±0.2% over the range of quantities of arsenic investigated.

It is believed that the factors limiting the accuracy of these titrations are: the oxidation of tripositive arsenic by atmospheric oxygen, the preparation and dilution of the standard solutions, the determination of the end point, and the measurement and control of the generation current.

Preliminary titrations of 70-microgram quantities of tripositive arsenic, over which no atmosphere of nitrogen was maintained, gave results as much as −0.6% in error. In addition, two groups of titrations (III) were made with the same stock solutions and carried out under as closely identical conditions as possible, except that the second group was not done under an atmosphere of nitrogen; the average value for the first group is 0.6 microgram greater than that for the second. These effects are attributed to air oxidation, and in all the other titrations shown in Table II an atmosphere of nitrogen was provided.

It is thought that a source of error in the above data was the accuracy with which standard solutions could be prepared. There is considerably better agreement between titrations within any one group than between the average titer of a group and the calculated value of the titer for that group.

The maximum spread in the values obtained for the blank time was 0.04 second for the high rate of generation and 0.2 second for the low rate. Two factors are involved in this spread: the accuracy with which the measurements and extrapolations could be made, and the random contamination of blank solutions. It is probable that essentially these same factors enter into the determination of the end point.

The accuracy to which the generation current could be determined was about ± 0.03%, and it could easily be controlled within this limit.

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Effect of Ammonium Salts on Determination of Nicotine

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Ammonium salts interfere in the determination of nicotine by the silicotungstic acid method by retarding the precipitation. Graphs are presented to show the effects of concentrations of nicotine, salt, and reagent and time of digestion on recovery of nicotine. Procedures are proposed to minimize the effect of the salt.

DETERMINATION of nicotine by the gravimetric silicotungstic acid procedure is the official method of the Association of Official Agricultural Chemists (*1*). However, if other alkaloids are present—for example, nornicotine—they are precipitated with nicotine and cause erroneously high results.

Ammonia, another volatile base, has not been considered a possible source of error in this determination, inasmuch as Chapin (*3*) stated that no precipitate was formed when silicotungstic acid was added to a solution containing ammonium chloride. In this laboratory, ammonia was assumed to have no effect until an attempt was made to determine nicotine in a solution that contained nicotine and a fairly high concentration of ammonium salts. When silicotungstic acid was added to this solution, no precipitate formed, either immediately or after the solution had stood overnight. After it had stood for 64 hours in a refrigerator, however, an appreciable precipitate formed, indicating that ammonium salts have a retarding effect on precipitation of nicotine. Consequently, experiments were undertaken to prove or disprove this effect and, if it exists, to determine its magnitude.

METHOD

A stock nicotine solution was prepared by placing a weighed amount of nicotine in a volumetric flask containing sufficient dilute hydrochloric acid to assure an acid solution after it was made to volume with water.

Aliquots containing from 10 to 100 mg. of nicotine were taken from the stock solution and placed in beakers. Four milliliters of hydrochloric acid (1 + 4) were added, and the solutions were diluted to make the volume 100 ml. after the addition of the requisite amount of 12% silicotungstic acid. One milliliter of this reagent was added for each 10 mg. of nicotine. The beakers were placed on a steam bath until the precipitate dissolved, or for 30 minutes, and the solutions were then kept in the refrigerator at about 5° C. for 18 hours, except when the conditions of the experiment required otherwise. The precipitates were collected in tared, ignited Gooch crucibles containing asbestos pads. The precipitates remaining in the beakers were loosened with a rubber policeman, quantitatively transferred to the crucibles, and washed well with dilute hydrochloric acid (1 + 1000). The precipitates were dried under infrared lamps and ignited in a muffle furnace, first at 650° C. for 2 hours and then at 800° C. for 15 minutes. The weight of the residue was multiplied by the theoretical factor 0.1141 to convert the weight of the oxides to the weight of nicotine.

This procedure differs from the A.O.A.C. official method in two respects: The precipitate is digested on a steam bath and then refrigerated overnight instead of merely standing at room temperature overnight, and ignited Gooch crucibles are used for filtering and igniting the precipitate rather than filter paper and platinum crucibles. Use of Gooch crucibles and suction speeds the filtration and eliminates possible errors due to the filter paper.

EXPERIMENTAL

Experiments were conducted in which the following conditions were varied: concentration of ammonium salts, time of standing, amount of silicotungstic acid, concentration of nicotine, and temperature.

Experiments were made with both ammonium chloride and ammonium sulfate in concentrations of 0.0 to 18.75%. The time of standing ranged from 18 to 88 hours. The amount of nicotine (about 10 mg.), volume of silicotungstic acid reagent, and temperature during standing (5° C.) were held constant. In each case, 4 ml. of 1 + 4 hydrochloric acid were added, and the final volume was adjusted to 100 ml.

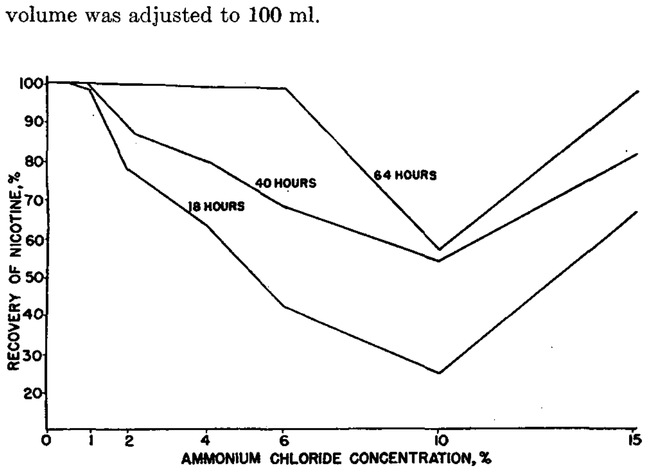

Figure 1. Effect of Concentration of Ammonium Chloride and Time of Standing on Recovery of Nicotine

In each series the amount of nicotine found when no ammonium salt was present was assumed to represent a 100% recovery, and all other recoveries were related to this. Figures 1 and 2 show the effects of time of standing and concentration of ammonium chloride and ammonium sulfate, respectively. A comparison of the two figures shows that the retarding or inhibiting effect of the sulfate salt occurs at a lower concentration, and, except for extremely low concentrations, is not eliminated by long standing. Recoveries for 88 hours (not shown in Figure 2) were essentially the same as for 64 hours.

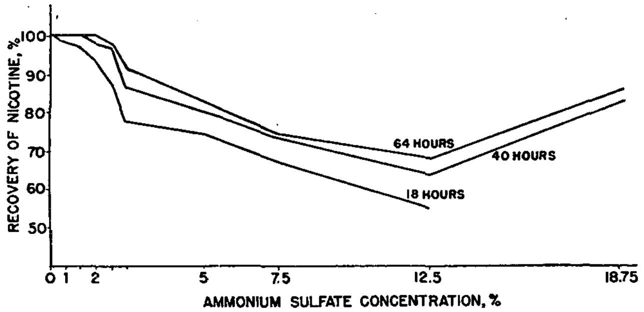

Figure 2. Effect of Concentration of Ammonium Sulfate and Time of Standing on Recovery of Nicotine

Figure 1 shows that as much as 6% ammonium chloride was tolerated if the solution was allowed to stand for 64 hours or longer. When it stood for 18 hours, the period designated in the A.O.A.C. method, 1% of ammonium chloride caused some reduction in recovery of nicotine, whereas 2% lowered it almost one fourth.

Figures 1 and 2 show that concentration of ammonium chloride and ammonium sulfate of 15 and 18.75%, respectively, caused the apparent recovery of nicotine to be greater than that obtained from solutions with 10% ammonium chloride and 12.5% ammonium sulfate. This was probably due to an accompanying coprecipitation of ammonium silicotungstate. That ammonium silicotungstate is precipitated from solutions of high ammonium salt concentration was confirmed by blank analyses on solutions containing 5, 10, and 15% ammonium chloride. Although no precipitate was formed in the 5% solution, there was an appreciable amount in the 10 and 15% solutions, which in terms of nicotine was equivalent to 8.5 and 10.7 mg., respectively. Therefore, solutions containing more than 5 or 6% ammonium chloride should not be analyzed by the silicotungstic acid method.

It was thought that the suppressing or retarding effect of ammonium salts might be avoided by increasing the ratio of silicotungstic acid to nicotine, even though this might involve establishing an empirical factor for converting the weight of the oxides to the weight of nicotine. Consequently, an experiment was conducted in which the amount of silicotungstic acid and the concentration of ammonium salt were varied. The amount of nicotine (10 mg. per 100 ml. of solution) and the time of standing at 5° C. (18 hours) were constant. By increasing the reagent from 1 to 4 ml. per 10 mg. of nicotine, recovery was increased (Figure 3). However, because recoveries at the various salt concentrations did not approach a constant value, a higher ratio of reagent to nicotine was eliminated as a possible remedy for the ammonium salt effect.

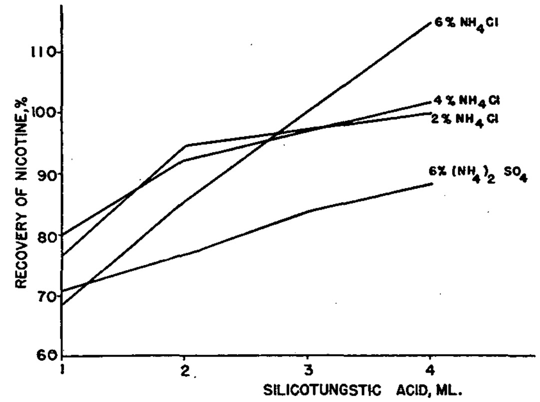

Figure 3. Effect of Concentration of Ammonium Salt and Volume of Reagent on Recovery of Nicotine

The A.O.A.C. method for nicotine analysis recommends that aliquots containing 100 mg. of nicotine be taken for analysis but states that as little as 10 mg. may be used. Because the allowable range of nicotine concentration is from 10 to 100 mg., the effect of ammonium salts was studied at different nicotine concentrations within this range. As shown in Figure 4, better recoveries were obtained at the higher nicotine levels, especially when ammonia was present as the chloride rather than as the sulfate. Complete recovery of nicotine from a 2% ammonium sulfate solution was not obtained even with 100 mg. of nicotine. The curve for ammonium chloride indicates that solutions containing more than 50 mg. of nicotine per 100 ml. can be analyzed satisfactorily with an 18-hour standing period at 5° C. even if they contain the maximum allowable amount (6%) of the salt.

Solutions containing 6% ammonium chloride and less than 50 mg. of nicotine per 100 ml. should not be analyzed by the regular method. There are two possible alternatives: allow the solutions to stand for 64 hours instead of 18, or remove ammonia or prevent its effect on the precipitation. The first alternative gave good recovery (Figure 1), but because of the excessive time required, a search was made for some means of accomplishing the second.

The temperature during standing was about the same (5° C.) for the experiments discussed thus far. Although there was not much hope that changing the temperature would eliminate the effect of the salt, the effect of temperature was studied. One set of solutions containing about 10 mg. of nicotine per 100 ml. was allowed to stand for 18 hours after precipitation at room temperature, and a second set was kept in a refrigerator at 8° C. The average weight of nicotine recovered was 9.87 mg. for the solutions at room temperature, as compared with 9.90 mg. at 8° C., indicating little or no effect of temperature in the absence of ammonium salts. In the presence of ammonium chloride, however, the corresponding weights—7.52 and 8.68 mg. of nicotine, respectively—showed that the effect of the salt is less pronounced at lower temperatures.

There was a possibility that a readjustment of the pH of the solution might aid in overcoming the effect of the salt. The optimum pH of the solution under normal conditions of analysis is about 1.1, both before and after precipitation of the nicotine. The ammonium sulfate had only slight buffering action, even in concentrations as high as 10%. Therefore the low results with ammonium salts are not due to a change in pH. Because the possibility remained that a pH of 1.1 was not optimum when ammonium salts were present, nicotine solutions containing ammonium sulfate were adjusted to pH 0.6, 1.0, and 2.0 and analyzed for nicotine. None of the recoveries was better than those obtained from similar solutions at pH 1.1. These results indicate that the effect of the salt cannot be suppressed by changing the conditions of the determination.

The possibility that formaldehyde would bind the ammonia, thus removing its effect, was then tested. Although higher nicotine recoveries were obtained from ammonium salt solutions when formaldehyde was added, apparent recoveries greater than 100% were obtained when no salts were present. Consequently, attempts to develop a method based on the use of formaldehyde were abandoned.

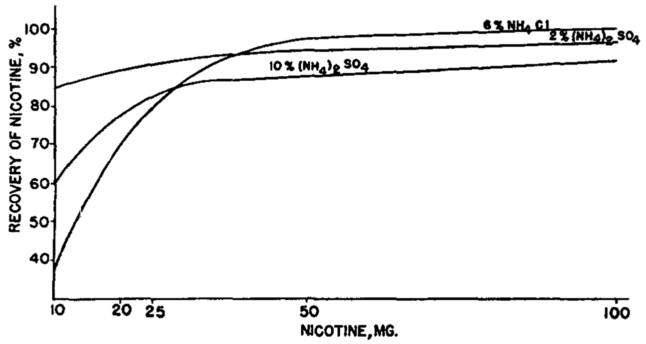

Figure 4. Effect of Amount of Nicotine and Concentration of Ammonium Salt on Recovery of Nicotine

There still remained the possibility of removing the ammonia from nicotine preparations before the distillation of the nicotine or before a redistillation. Markwood (*6*) and Bowen and Barthel (*2*) reported methods for separating nicotine, a tertiary base, from nornicotine, a secondary base, by reaction of the latter with nitrous acid. Because ammonia also reacts with nitrous acid, it was hoped that ammonia could be destroyed in the nicotine solutions without affecting the nicotine; however, such was not the case. At room temperature and below, the reaction of ammonia with nitrous acid or the decomposition of the ammonium nitrite was negligible; at temperatures high enough to decompose the ammonia, the nicotine also reacted with the nitrous acid, with the result that recoveries were lower than those obtained in the presence of ammonium salts.

Treatment of the nicotine-ammonia solution with a hydrogen ion exchange resin was tried to determine whether a preferential adsorption of ammonia or nicotine might be effected, but this has not been successful. Neither a fractional distillation from an ethylene glycol solution according to the method of Libmann-Métayer (*4*) nor the fractional distillation from a phosphate buffer solution as recommended by Neimark (*7*) led to complete recovery of nicotine.

Nicotine solutions containing high ammonium salt concentrations were analyzed by the method described by Markwood (*5*), but apparent nicotine recoveries exceeded 100% when as little as 0.05% ammonium chloride was present.

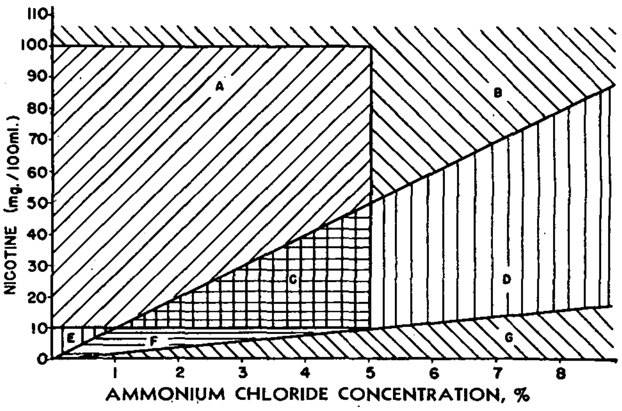

Figure 5. Nicotine Solutions for Which Various Analytical Treatments Are Recommended

The question arose: Was this effect on the precipitation of nicotine silicotungstate peculiar to ammonium salts or was it a general salt effect? Consequently, nicotine solutions containing different amounts of sodium sulfate were analyzed by the silicotungstic acid method. The recoveries paralleled those shown in Figure 2 for ammonium sulfate. Therefore, the low nicotine recoveries from solutions containing ammonium salts are the effect of a salt rather than something peculiar to the ammonium ion. Most of the studies were made with ammonium salts, because they are most likely to be encountered in work with nicotine and because nicotine can be separated from other common salts by steam distillation from an alkaline solution.

SUMMARY

The findings reported here can best be summarized by the schematic diagram, Figure 5. Any solution with nicotine and ammonium chloride concentrations which falls in area A can be analyzed by the Association of Official Agricultural Chemists' procedure, with 18 hours' standing at 5° C. If the nicotine–ammonium salt concentrations fall in area B, the solution must be diluted until area A is reached; the procedure for area A then is used. If a point in area C represents the solution, the analysis should proceed as usual, except that the time of standing at 5° should be at least 64 hours. Solutions represented by points in area D need only be diluted and treated according to the procedure for area C. Solutions whose point falls in area E or F must be concentrated until they are characterized by points in area A or C, respectively, and treated according to the procedure for that area. If characterized by a point in area G, the solution cannot be analyzed by the silicotungstic acid method with accuracy.

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Determination of Liquid-Vapor Equilibria

New Dew Point–Bubble Point Apparatus

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A new form of dew point–bubble point apparatus is suitable for determining the liquid-vapor equilibria of binary systems which are liquid at room temperature and atmospheric pressure. The technique of operation and the theory and method of deriving both the individual dew points and bubble points and the total dew point curve and bubble point curve are given. Suitability of the dew point–bubble point apparatus for obtaining liquid-vapor equilibria was established by reproducing closely the results obtained by Scatchard on the methanol-benzene system. The method is advantageous because only small amounts of reagents are needed for the complete determination of a system; no analyses are required; identical solutions are run at each temperature; and the independent determination of the dew point curve allows the selection of evenly spaced points at desired concentrations. Possible application of apparatus is in determination of molecular weights of liquids, analysis of binary liquid systems, and study of liquid-vapor equilibria of ternary and higher order systems.

APPARATUS designed to determine bubble points and dew points has been used for many years to study the phase behavior of hydrocarbons in petroleum. In nearly all instances, this work has been done on substances of low molecular weight, such as methane, ethane, etc., which are ordinarily gases or low boiling liquids. The apparatus generally used was constructed of metal which could be employed at very high pressures, inasmuch as data up to the critical point were commonly desired. The work done by Sage and Lacey (*2*) is typical. In some instances, glass capillary apparatus was used (*1*).

Systems which are liquid at room temperature have not been studied with apparatus such as those mentioned. The dew point–bubble point apparatus constitutes a new form which utilizes essentially the same basic principles as the types referred to above, but is specifically adapted to examine systems which are liquid at room temperature and atmospheric pressure.

THEORY OF THE METHOD

A generalized liquid-vapor diagram of a binary system which forms a minimum boiling mixture is given in Figure 1. The data are plotted at constant temperature; if they were plotted at constant pressure a somewhat similar, inverted curve would be obtained.

The horizontal line, *MN*, is a tie line connecting phases *M* and *N*, which are in equilibrium with each other. The usual forms of apparatus used for obtaining liquid-vapor equilibrium data are designed to determine points *M* and *N* simultaneously. After a series of such tie lines has been determined along the entire range of concentration, a line is drawn through all the points analogous to *M* to give the "liquid curve," and a line is drawn through the points analogous to *N* to give the "vapor curve."

Examination of Figure 1 shows that the diagram could also be produced by joining the end points of a series of vertical lines such as *RM*. This is not a tie line; it is merely a constant composition line which describes what happens to a mixture of a given composition as the pressure on it is changed at constant temperature. For a sample having the composition N_A and a pressure greater than P_1, the system will consist of a liquid phase only. As the pressure is lowered, the vapor pressure becomes equal to the external pressure at P_1, and an infinitesimal amount of vapor which is in equilibrium with the liquid is formed. This is known as the bubble point, *M*. Further lowering of the pressure results in two phases which constantly change in relative amounts; the liquid phase decreases while the vapor phase increases until pressure P_2 is reached. At this point, an infinitesimal amount of liquid in equilibrium with the vapor remains, and now the vapor has the same composition as the original liquid. This point is known as the dew point, *R*, because when it is approached from the opposite direction, it represents the point at which initial condensation takes place. By joining all the points analogous to *M*, the "bubble point (liquid) curve" is produced. Connection of all the points corresponding to *R* gives the "dew point (vapor) curve."

APPARATUS AND OPERATION

Figure 2 shows the apparatus, which was designed according to the principles discussed above. It is of all-glass construction and has three major parts.

A is the body of a 500-ml. graduated cylinder, which ends in a gradual taper at the top, culminating in a capillary. This arm serves as the vaporizing chamber.

B is a large mercury reservoir.

C is used for balancing the mercury height in *A*. It is made of 10-mm. tubing to minimize meniscus errors. When the levels of the mercury in *A* and *C* are equal, the pressure in the vapor space of *A* is equal to that of the manometer, which is connected in series with *C*. Correction for the pressure due to the weight of the sample is −0.1 mm. of mercury per milliliter. In constructing

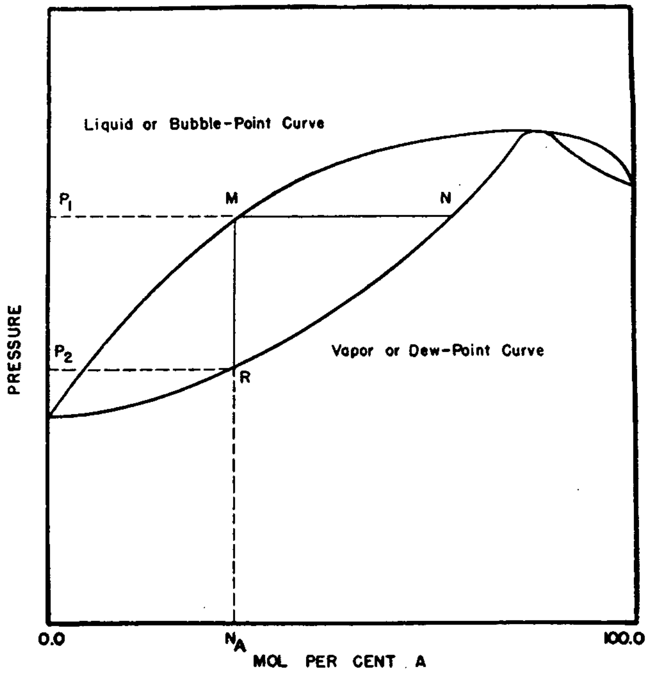

Figure 1. Dew Point–Bubble Point Curves for Generalized System with Minimum Boiling Azeotrope

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the apparatus, *C* is placed as close to *A* as possible in order to increase the accuracy of matching the mercury levels of *A* and *C*.

The entire apparatus is immersed in a constant temperature bath, *L*, in which water is maintained at the level indicated by the dotted line passing through stopcocks *E*, *F*, and *G*. The apparatus is supported in the bath by a ringstand and clamp combination which is also located within the bath. A split rubber tube is fitted on the bottom arm, which rests on cork stoppers to cushion the weight of 20 pounds (9 kg.) of mercury. The introduction of samples, vaporization, balancing of mercury, etc., are all accomplished by balancing vacuum and atmospheric pressure through the suitable adjustment of the various stopcocks.

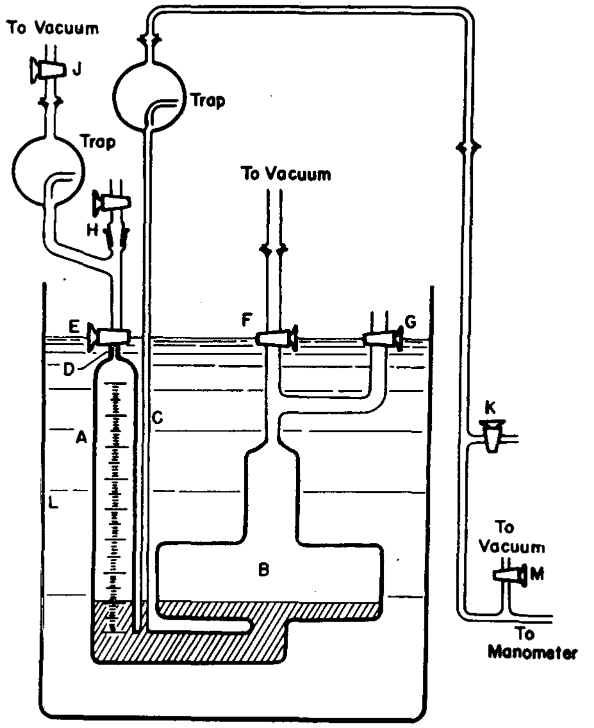

Figure 2. Dew Point–Bubble Point Apparatus

The 7-gallon (26.5-liter) thermostat is held to within ±0.02° C. of the operating temperature, which is a smaller variation than the average error in reading pressure. An absolute manometer with attached graduated scale capable of ±0.2-mm. accuracy is used for pressure readings. The vacuum source for the system consists of a mechanical pump which is connected to a 5-gallon bottle and a 3-gallon bottle, which act as vacuum reservoirs. These are used as the operating source of vacuum and allow good control over pressure changes in the system. The vaporization chamber and the mercury reservoir are connected with the 5-gallon bottle, while the manometer arm is connected with the 3-gallon bottle. A complete system of stopcocks and T-tube connections within the pump-reservoir system allows separate control over each part of the apparatus.

The procedure for making a run is as follows:

After the bath has come to temperature, the mercury in *A* is forced up to a point just above stopcock *E*, which is then closed. The apparatus is opened to the atmosphere at *H*, *G*, and *K*. Plug *H* is removed, a sample somewhat larger than will be used is introduced by means of a hypodermic syringe, and *H* is replaced. By carefully opening *E*, the mercury which is above it and also the proper amount of sample varying from 1 to 5 ml. are drawn into *D* and into the tapered part of *A*, and the stopcock is closed. With *E* closed, *J*, *F*, and *M* are opened to vacuum in such a way that the liquid in *A* forms about 300 ml. of vapor. *C* and *B* are then brought to atmospheric pressure. This causes condensation in *A* and brings the liquid line to a point just below *D*. The bubble above the liquid represents air which has been dissolved at atmospheric pressure. By carefully opening *E* to vacuum, this bubble, plus a small amount of liquid, is forced up above *E*, which is then quickly shut off. Thus, the trapped liquid is left fairly free of dissolved gases. This degassing procedure is followed only when obtaining bubble points; dissolved air in the very small dew point samples has no effect on the dew points.

With the sample at temperature, the mercury in *C* is held at a level approximately the same as the top of *A* while the pressure in *B* is gradually lowered until a volume of 20 to 30 ml. of vapor forms in *A*. The mixture in *A* is brought to equilibrium by swirling the liquid with a rocking motion of *A*. Then the mercury levels in *A* and *C* are equalized by matching the reflection of the mercury in *C* on tube *A* with the mercury in *A*, and a reading on the manometer is taken. The pressure in *B* is again lowered a little to allow 25 ml. more of vapor to form, and the above procedure is repeated. In dew point determinations a 0.01- to 0.1-ml. sample is used and no swirling is employed to attain equilibrium. In both bubble point and dew point determinations equilibrium is usually reached in 1 or 2 minutes, as indicated by a constant pressure reading.

A series of volume and pressure readings is obtained, which can be plotted against each other. From the curves obtained in this way, the bubble points and dew points are determined. Some typical individual bubble and dew point determination curves are shown in Figure 3. In curves *a* and *b*, extrapolation of the volume *vs.* pressure curve back to the pressure axis gives the bubble point (*B.P.*) of the initial mixture. In curves *c*, *d*, and *e*, the dew point is located where the change of slope indicates that all the liquid has vaporized, and the vapor is expanding as a gas. These points are indicated by *D.P.*

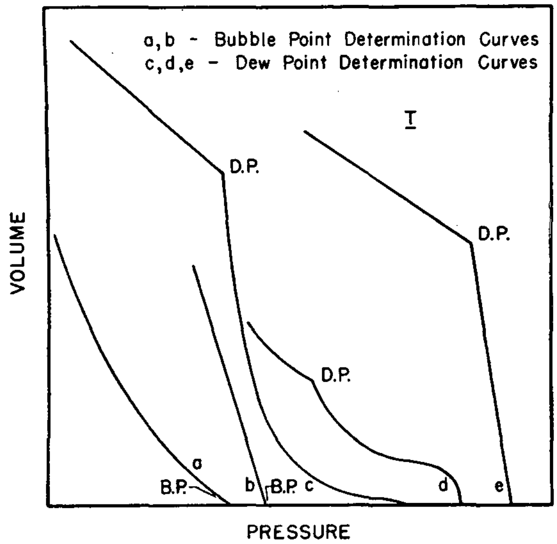

Figure 3. Generalized Volume *vs.* Pressure Curves for Determination of Dew Points and Bubble Points

The present form of the apparatus is suitable for the pressure range 0 to 1 atmosphere and for temperatures up to about 50° C. By replacing the vacuum pump with a pressure pump the range of pressure may be increased to several atmospheres with a probable revision of the equipment employed for sample introduction. The temperature range could probably be increased to well over 100° C. if the bath liquid were properly changed and extensions placed on the stopcocks, which are immersed in the liquid surface, to avoid burning the operator's hands. Corrections for the vapor pressure of mercury should be made for any temperature above 80° C.

ACCURACY OF APPARATUS

The suitability of the apparatus for obtaining liquid-vapor equilibria was established by repeating the work of Scatchard and co-workers (*3*) on the methanol-benzene system. The reasons for choosing this system were twofold: It is similar to the methanol-toluene system for whose determination the apparatus was

Table I. Composition of Methanol-Benzene Solutions Made Up at 25° C.

Vol. of CH_3OH *Ml.*	Vol. of Benzene *Ml.*	CH_3OH *Mole %*	CH_3OH (Scatchard) *Mole %*
0.63	9.43	12.8	13.02
1.71	8.29	30.7	31.07
3.14	6.93	49.8	49.89
3.30	6.70	51.9	51.91
4.41	5.60	63.2	63.05
6.45	3.54	80.0	79.65
8.40	1.60	91.8	91.97

Table II. Dew Points and Bubble Points of Methanol-Benzene System at 35.0° C.

CH_3OH in Liquid *Mole %*	Dew Point *° C.*	Bubble Point *° C.*
0.0	...	149.4
12.8	164.5	276.2
30.7	206.5	288.4
49.8	280.0	292.7
63.2	289.0	292.8
80.0	244.0	283.1
91.8	222.0	255.8
100.0	...	209.9

originally developed; and the accurate results of Scatchard *et al.* provided a good standard for comparison.

The reagents were distilled through a fractionating column and their vapor pressure was checked at 34.97° ± 0.02° C. The values obtained were almost exactly the same as given by Scatchard. Seven solutions were made up corresponding as closely as possible to the compositions used by Scatchard. Pertinent data are given in Table I. The solutions were run in the apparatus, and the data obtained are given in Table II. A diagram of the methanol-benzene system at 35.0° C. as drawn from the data of Scatchard is shown in Figure 4. The data obtained by the apparatus were superimposed on the diagram as indicated by the legend.

Examination of the bubble point data shows very good agreement. The dew point data do not appear to be in as good agreement, a condition which may be due to the relatively few points used to delineate the curve. In any case, the results justified going on to determine the liquid-vapor equilibrium data for the methanol-toluene system, which will be reported in a forthcoming paper.

APPLICATIONS

There are three applications of the dew point–bubble point method and apparatus.

Molecular Weights. The accurate determination of molecular weights should be possible. For this purpose, it would be necessary to incorporate a microvolumetric bulb into the apparatus for measuring a very small liquid sample to be completely vaporized. The density of the liquid is determined at the same temperature with a pycnometer using a separate, larger sample. Thus the weight of samples used can be found. The sample is completely vaporized, and a series of values of V and P in the vapor state is obtained. From these, an accurate value of molecular weight can be obtained by the method of limiting densities according to the formula:

$$M = RT\left(\frac{d}{P}\right)_{P\,=\,0}$$

where $\left(\frac{d}{P}\right)_{P\,=\,0}$ is the limiting value obtained when $\frac{d}{P}$ is plotted against P and extrapolated to $P = 0$. R is the gas constant, and T is the absolute temperature.

Analysis. Often binary mixtures are encountered which are difficult to analyze by refractive index or density. If the liquid-vapor diagrams of such mixtures were accurately known, they could be analyzed by determining the bubble point and dew point of a given sample. Because each pair of points corresponds to a particular composition, the correct value can be picked out on the diagram. In many instances, the same small sample will be satisfactory for determining both bubble and dew points, thus allowing economy in size of sample and time for determination.

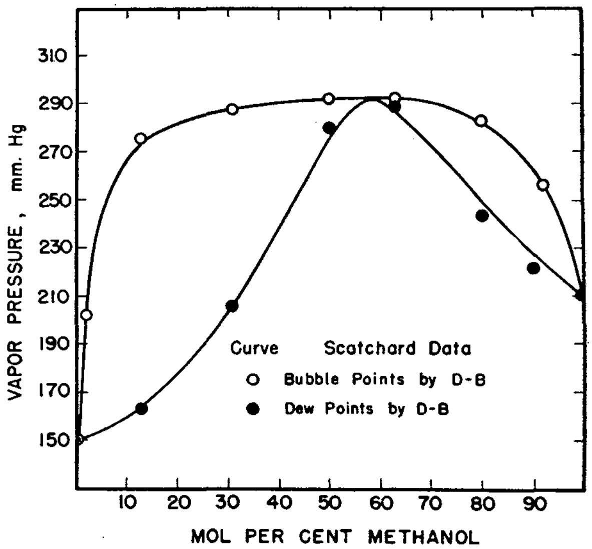

Figure 4. Methanol–Benzene System at 35.0° C.

Ternary Systems. The determination of liquid-vapor composition data for higher order systems has been heretofore avoided because of the difficulties of analysis. A method such as that suggested, where use of synthetic samples of known composition eliminates the need for analysis, should make the determination of these systems much less difficult.

CONCLUSIONS

Some of the important advantages of the dew point–bubble point method are: Small amounts of reagents may be used for the complete determination of a system. No analyses are required, because all samples are made up to accurately known compositions.

Identical solutions of a given composition can be used for each temperature at which a system is determined.

The independent determination of the dew point curve allows the selection of evenly spaced points at desired concentrations rather than leaving them to chance. Points close to the origin on each curve may readily be determined, so that the manner in which the bubble point and dew point curves come together in this region may be accurately delineated.

The apparatus should be applicable to the determination of molecular weights of liquids, to the analysis of binary liquid systems difficult to analyze by refractive index, density, etc., and to the study of liquid-vapor equilibrium data for ternary and higher order systems.

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Automatic Precision Glass Electrode

pH Measurement with a Vibrating Reed Electrometer

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Using a vibrating reed electrometer as detector, the potentials of glass-electrode assemblies were recorded on a strip-chart recorder. The precision of the measurements is approximately that of a Type K potentiometer and the reproducibility is sufficiently high to make it feasible to determine acidities of solutions to better than 0.1% under favorable conditions.

THIS paper describes the use of the vibrating reed (also called dynamic condenser or capacitative commutator) electrometer for high precision pH measurements with glass electrodes. The instrument may be used with a strip-chart recorder and the voltage sensitivity attainable is determined by the accuracy of the auxiliary potentiometer, which in this work has been a Leeds & Northrup Type K potentiometer. LeCaine and Waghorne have described a vibrating reed electrometer for ionization current measurements (*3*). Scherbatskoy and co-workers used a similar instrument (*5–7*) for radioactivity measurements in oil-well logging, where an instrument of high current sensitivity, great ruggedness, and adaptability for automatic operation was desired. A detailed study of this instrument has been made by Palevsky and co-workers (*4*), who also made certain design changes and improvements. All the authors point out that the instrument can be used for potential measurements in high resistance circuits.

This instrument appeared to be ideally suited for voltage measurements of glass-electrode assemblies and was expected to be a considerable improvement over the usual vacuum-tube electrometers, inasmuch as it appeared to combine great ruggedness and freedom from zero drifts with high sensitivity, adaptability for automatic recordings, and complete 110-volt alternating current operation. Since its first tests several years ago as a recording precision high impedance potentiometer, the instrument has been used routinely for precision potential measurements in this laboratory (*1*, *2*), and for potential measurements in low resistance circuits as well.

APPARATUS

Electronic Equipment. The vibrating reed electrometer is essentially a high resistance direct current voltmeter which is capable of measuring voltages in circuits of resistance up to 10^{15} ohms. Because the direct current potential is converted to an alternating current voltage by the "chopper" or dynamic condenser, a stable alternating current amplifier can be used in a 100% feedback system. In this manner the vibrating reed operates as a null type instrument where variations in the amplifier gain or in power supply voltages do not contribute to zero drift. With proper design the sensitivity is limited only by the noise produced by the thermal agitation in the input circuit. The zero drift, which is due to the changes of contact potential of the dynamic condenser surfaces, is usually about 0.1 mv. in 24 hours.

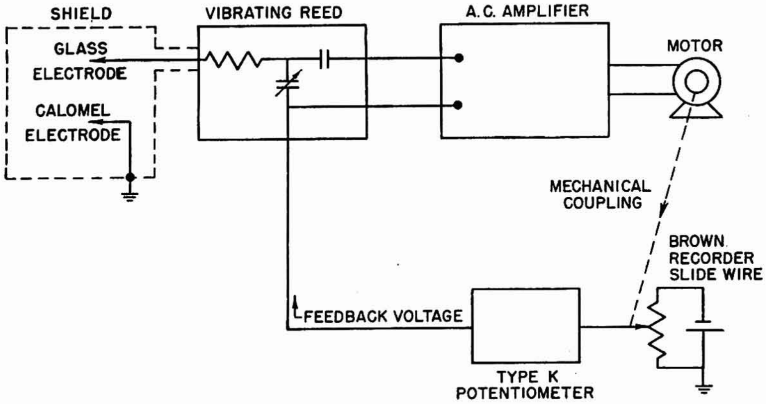

Figure 1. Block Diagram of Vibrating Reed Assembly

The block diagram in Figure 1 shows a typical self-balancing 60-cycle vibrating reed. When a voltage appears across the dynamic condenser input, an alternating current voltage is generated and amplified by the alternating current amplifier. The output of the amplifier drives a motor, which in turn adjusts the potentiometer to the null position. The indicated voltage on the self-balancing potentiometer is equal to the input voltage. In this way completely automatic recording of the potentials is made. Where maximum precision is required, the recorder slide wire should balance only a small fraction of the total cell potential—e.g., 3 or 10 mv. full scale—while the major fraction of the cell potential is balanced manually by a high precision potentiometer—e.g., Rubicon Precision potentiometer or L. & N. Type K-2 potentiometer. Because this potentiometer is on the low impedance side of the circuit, it need not be shielded. Calibration of the potentiometer can readily be achieved with the same circuit. The potential of a standard cell is fed into the vibrating reed input and its potential is balanced against the output of the potentiometer, whose dials are set for the nominal voltage of the standard cell. The Brown recorder is used as a null indicator.

Figure 1 does not represent a unique circuit and certain variants are possible—for example, the Type K potentiometer can be placed between the calomel cell and ground, or a 300-cycle reed with electronic feedback may be used.

The construction of the dynamic condenser requires considerable skill, especially in the preparation of the condenser surfaces where it is important to obtain low and stable contact potentials.

Both so-called "60-cycle" (*7*) and "300-cycle" reeds (*8*) have been used. Because in the former case the reed is driven by standard 60-cycle, 110-volt alternating current, the Brown amplifier can be used directly with only minor changes, such as removal of the "chopper" and addition of a preamplifier. If a recorder is to be used, the design of the 60-cycle reed is in general much simpler than that of the 300-cycle reed, for which a special oscillator and a separate amplifier and detector are needed. The 300-cycle reed requires more maintenance in general than the 60-cycle reed. Nevertheless, most of the measurements reported here have been carried out with the 300-cycle reed. A photograph of the complete assembly, using a 300-cycle reed, is shown in Figure 2.

In all earlier measurements the Brown recorder was adjusted to give 10-mv. full-scale deflection, and thus a reading accuracy of 0.01 to 0.02 mv. More recently recorders with full-scale sensitivity of 3 mv. have been used (giving a reading accuracy of 0.003 to 0.006 mv.). Although it appears that from the point of view of noise level still greater sensitivity could be used—e.g., 1 mv. full scale—the reproducibility of the measurements does not seem to warrant this at present, particularly in view of the fact that with this sensitivity the instrument would need considerably more attention in kinetic studies where the changes of potential with time are of interest.

Shielding. Aside from connecting cables, shielding is needed only for the glass-electrode assembly. This can be readily achieved by enclosing the cell and electrodes in an aluminum box.

Temperature Control. Temperature control of the cell within the box was achieved by placing it through a cover in a Dewar flask, filled with water. The temperature within the Dewar was maintained at the proper temperature by placing in it a copper coil through which thermostated water was pumped. This arrangement did not cause troubles in the detecting circuit, provided the coil was grounded to the case.

The cells were at first coated with paraffin on the outside. However, omission of such coating did not appear to influence the results

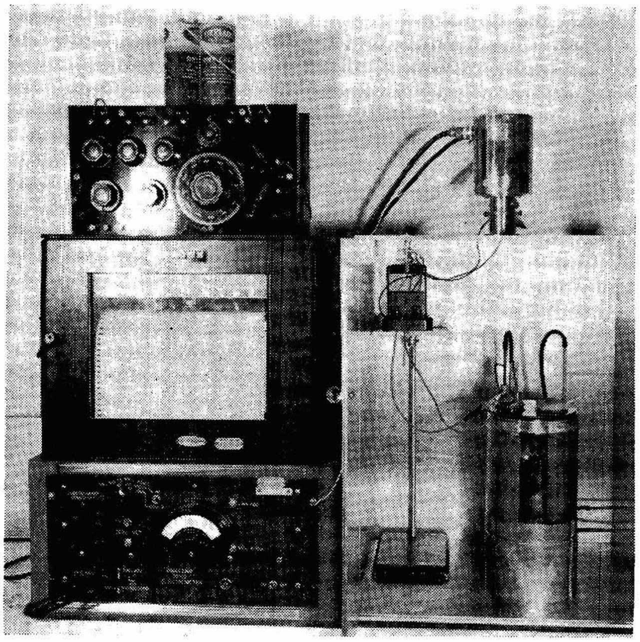

Figure 2. Vibrating Reed Electrometer Assembly for pH Measurements

Because careful temperature control of the calomel electrode appeared of importance, some calomel electrodes were specially assembled in small Dewar flasks as illustrated in Figure 3. These electrodes maintained temperature very well, if the room temperature did not drop below the temperature of the assembly. When this occurred, the temperature of the assembly dropped rapidly, presumably because of convection currents in the salt bridge projecting beyond the Dewar. The assembly returned to its original temperature only very slowly, even if continuously immersed in a thermostat. Careful insulation of the salt bridge and total immersion in a thermostat when not in use circumvented this complication reasonably well.

Electrodes. Most experiments were carried out with standard Beckman electrodes—calomel electrode No. 270 and glass electrode No. 290. Because measurements of potentials in circuits having resistances as great as 10^{12} ohms can readily be made, glass electrodes of resistance very much higher than the usual approximately 10^8 ohms could probably be used.

RESULTS

In a cell of the type used in pH measurements, the precision and reproducibility are determined by a number of factors aside from the characteristics of the electronic circuit. These are primarily the response of the measuring electrode, reproducibility of the liquid junction potentials, and drift in the reference potential. It was found that these factors are considerably more important than the characteristics of the measuring circuit, which is very fast, reproducible, and free of drift as indicated by measurement of the potential of a standard cell.

The potentials of glass-electrode assemblies often show prolonged drifts which may last from a few minutes to several hours and may be as high as several millivolts. It is believed that these drifts are due to changes in the liquid junction potentials with time, or changes in the characteristics of the glass electrodes. If the glass electrodes have been aged at not too high an acidity—i.e., in 0.01 *M* hydrochloric acid—they usually do not contribute appreciably to the drift. This can be demonstrated by measuring potentials in a cell without liquid junction—i.e., consisting of two well-aged glass electrodes—where such drifts are negligible. Similarly, the prolonged drifts can often be eliminated by replacement of the calomel assembly. It appears that these drifts become prominent if the flow rate of the calomel "electrodes" through the asbestos wick is too small. For the measurements reported here the calomel electrodes were selected for low drift.

The generally accepted technique of using glass electrodes involves their standardization (preferably at two points) before measurement. Thus, glass electrodes are usually used to establish differences in acidities rather than absolute values. By strictly following this procedure the sensitivity of the instrument can be utilized fully without special precautions, as shown in Table I.

The data for Table I were compiled by making a series of consecutive measurements in an air-conditioned room whose temperature was 25° ± 1° C. No other attempts were made to control temperature. The potential of the cell containing 0.01013 *M* hydrochloric acid was followed until it was constant, 0.4992 ml. of 0.1000 *M* hydrochloric acid was then added, and the resulting potential change was recorded. The cell was then cleaned and the measurements were repeated. It may be noticed from Table I that the potential changes (ΔE) thus attained show a considerably smaller standard deviation (σ) than the various readings for the same acid. (σ was calculated according to the equation $\sigma = \sqrt{\frac{(\bar{x} - x)^2}{(n - 1)}}$ where n is the number of

Table I. Potential of Glass-Calomel (Saturated Potassium Chloride) Electrode Assembly without Special Temperature Control

T = 25° ± 1° C.
E_i = potential (mv.) in 0.01013 *M* HCl
E_f = potential (mv.) after addition of 0.4992 ml. of 0.1000 *M* HCl to 15 ml. of 0.01013 *M* HCl
Brown recorder, full-scale sensitivity 10 mv.

	E_i	E_f	ΔE
1	332.52	338.97	6.45
2	332.36	338.84	6.48
3	332.28	338.74	6.46
4	332.30	338.72	6.42
5	332.35	338.79	6.44
6	332.38	338.79	6.41
7	332.39	338.86	6.47
8	332.30	338.78	6.48
9	332.46	338.96	6.50
10	332.44	338.90	6.46
11	332.51	339.00	6.49
12	332.61	339.02	6.41
Av.	332.41	338.86	6.456
σ	0.10	0.10	0.032

Table II. Potential of Glass-Calomel (Saturated Potassium Chloride) Electrode Assembly with Temperature Control

Alternating measurements of two acids. A. 0.01003 *M* HCl. B. 0.00439 *M* HCl
Solution temperature 25.10° ± 0.05° C.
Brown recorder, full-scale sensitivity 3 mv.

Date	*A*	*B*	ΔE
5/15	331.220	310.034	21.186
	331.205	309.997	21.208
	331.205	310.037	21.168
	331.165	310.003	21.162
	331.153	309.970	21.183
	331.156	309.961	21.195
	331.159	309.973	21.186
	331.159	309.967	21.192
	331.144	309.961	21.183
	331.138	309.958	21.180
5/17	331.058	309.891	21.167
5/18	331.263	310.104	21.159
	331.278	310.083	21.195
5/25	331.281	310.086	21.195
5/26	331.296	310.107	21.189
	331.424	310.241	21.183
	331.378	310.205	21.174
5/27	331.083	309.893	21.189
Av.	331.209	310.026	21.183
σ	0.096	0.096	0.013

observations, $\bar{x}$ the arithmetrical average, and x the observed value.) Because σ for ΔE was only slightly larger than the estimated reading error (10 mv. full scale), it appeared that recording at a smaller value for full-scale sensitivity would further lower the standard deviation of the readings.

A similar set of data, determined at a full-scale sensitivity of 3 mv., is shown in Table II. For these data the cell was thermostated as described above. The recorded measurements represent the alternate measurements (to equilibrium) of 0.01003 *M* and 0.00439 *M* hydrochloric acid solutions over a period of 2 weeks using the same electrodes. The "absolute" readings showed a standard deviation σ = ca. 0.1 mv., while the differences showed the very low value $\sigma = 0.013$.

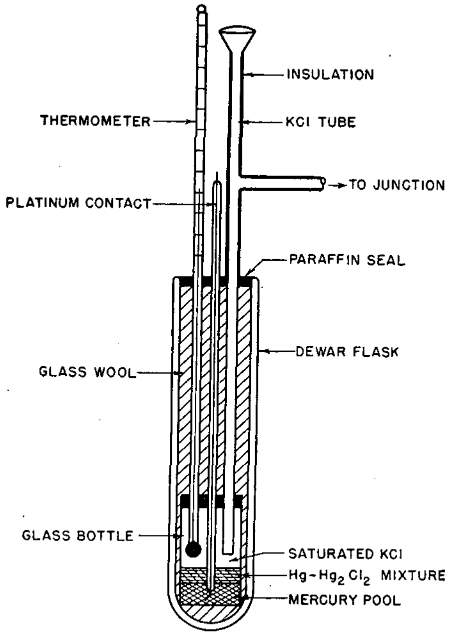

Figure 3. Calomel Half-Cell in Dewar Flask

It is believed that the rather large values of σ for the absolute measurements are mainly due to inadequate thermostating of the calomel electrode. For this reason a calomel half-cell, built in a small Dewar flask as described above, was used for a series of similar measurements (Table III) using a recorder of 10-mv. full-scale sensitivity. For this series of measurements the solutions again were alternated and the series was completed in one 8-hour period. The standard deviations for the absolute readings were only 0.025 mv., in close agreement with the error for the differences (ΔE) of the measurements in this series as well as the series in Table I.

Inasmuch as the standard deviation for the measurement of potential differences is rather low (under favorable circumstances ±0.015 mv.), it appears feasible to determine the concentration of acids by glass-electrode pH measurements directly without need for titration, provided all other variables are carefully controlled and standardized. This may be of particular interest for solutions containing hydrolyzable ions. If the permissible analytical error is 0.1%, a total error in the potential measurements of ca. 26 μv. can be tolerated. As can be seen from Table II, this is almost twice the standard deviation which can be attained.

Table III. Potential of Glass-Calomel (Saturated Potassium Chloride) Electrode Assembly with Special Temperature Control of Calomel Cell

Alternating measurements of two acids. A. 0.01004 *M* HCl. B. 0.005025 *M* HCl
Ionic strength. 0.5 (KCl)
Temperature. 24.67° ± 0.03° C.
Brown recorder, full-scale sensitivity 10 mv.

	0.01004 *M* H_3O^+		0.005025 *M* H_3O^+	ΔE
1	330.74	2	313.45	17.29
3	330.76	4	313.43	17.33
5	330.75	6	313.43	17.32
7	330.75	8	313.46	17.29
9	330.80	10	313.45	17.35
11	330.75	12	313.40	17.35
13	(330.29)	14	313.38	....
15	330.73	16	313.45	17.28
17	330.72	18	313.43	17.29
19	330.75	20	313.42	17.33
21	330.76	22	313.40	17.36
Av.	330.751[a]		313.427	17.319
σ	0.021[a]		0.025	0.030

[a] Average calculated excluding 13.

For proper use of the glass electrode for measurement of the acidity of solutions, it is necessary to determine the Nernst slopes (potential change of assembly for a tenfold change in oxonium ion activity) in the acid systems under consideration. These slopes (which at 25° C. should be 59.15 mv.) were found to be close to this value (at constant ionic strength) for most electrodes at low acidity, as shown in Table IV, which represents data simultaneously obtained in a cell containing three glass electrodes and a calomel reference electrode. Because the ionic strength of the solutions remained constant and the concentration of oxonium ions was small compared with the ionic strength, the slopes were calculated assuming that the activity coefficients of the oxonium ions and the liquid junction potentials are the same for the two solutions.

Some data on Eimer and Amend standard buffers of nominal pH 4.00 ± 0.01 and 7.00 ± 0.02 have been included. The Nernst slopes are somewhat high, the deviation from the theoretical value being outside the experimental error.

The close agreement between the various glass electrodes which is described in Table IV is somewhat misleading, because, at least at higher acidity and high ionic strength, definite deviations of the electrodes from each other become apparent.

Measurements of potential differences for different acids using the same glass electrode and different calomel electrodes are shown in Table V. The data were obtained again simultaneously for the three combinations of electrodes and it can be seen that the potential differences found are independent of the particular calomel electrode used.

Table IV. Nernst Slopes for Various Glass Electrodes

Brown recorder, full-scale sensitivity 3 mv.
$T = 25.00° \pm 0.05°$ C.

Glass Electrode	*E*, Mv.			
	0.010029 *M* HCl 1.00 *M* Cl^- (KCl)	0.004391 *M* HCl 1.00 *M* Cl^- (KCl)	ΔE, Mv.	Slope, Mv./pH
1	342.735	321.542	21.193	59.08
2	361.332	340.214	21.118	58.87
3	389.677	368.570	21.107	58.84
	E & A Buffers			
	pH 4.00	pH 7.00		
1	232.38	49.84	182.54	60.84
2	251.82	69.20	182.62	60.87
3	280.14	97.52	182.62	60.87

Table V. Influence of Calomel Cell on Nernst Slopes

[Ionic strength 0.5 (KCl)]

Calomel Electrode	*E*, Mv.				Recorder Full Scale, Mv.
	0.01003 *M* HCl	0.004391 *M* HCl	*E*, Mv.	Slope, Mv./pH	
1	342.927	321.839	21.09	58.96	3
2	342.848	321.732	21.12	59.04	3
3	342.604	321.528	21.08	58.93	3

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It is a pleasure to acknowledge the assistance of J. East and O. C. Cole in assembling and maintaining the instruments. The authors are indebted to the Instrument Divisions of the Metallurgical Laboratory of the University of Chicago (now Argonne National Laboratory) and of the Oak Ridge National Laboratory for the reeds and amplifiers.

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SURFACE CHROMATOGRAPHY

Refinements in Apparatus and Technique

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By means of an extended technique and improved designs in pipet construction for surface chromatography a useful variable, the ratio of developer volume to sample volume, is automatically controlled. By fixing this ratio at appropriate values and relating it to the extent of migration of a zone the chromatographic behavior of a given solute may be accurately appraised. Details of a superior ripening technique and of pipet construction and calibration are given.

THE sample pipet previously described for use in surface chromatography (*3*), and shown in Figure 1,*a*, has the disadvantage of being fragile and easily broken. A more rugged pipet patterned after that of Anderson (*1*) was prepared (Figure 1,*b*) to eliminate this difficulty but was found to have certain other drawbacks. The weld at point *k* must be carefully formed and thoroughly annealed in order to prevent the occurrence of excessive strains. Furthermore, when the delivery tip is drawn out to satisfactory outside dimensions the bore suffers reduction in size beyond practical limits. The construction shown in Figure 1,*c*, however, resolves these problems and is readily drawn from 7-mm. tubing of either heat-resistant or soft glass. Its preparation may be visualized by reference to Figure 2.

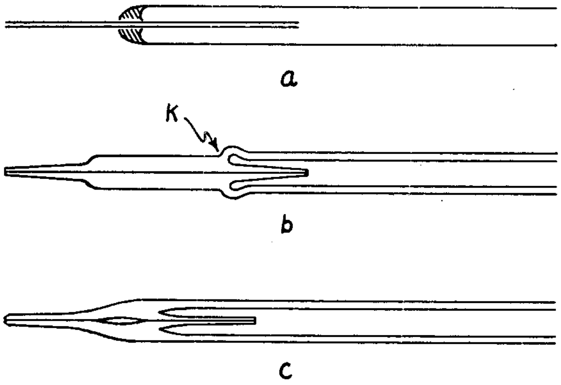

Figure 1. Sample Pipets

The bulb, *a*, is drawn from the same tubing as *b*. In drawing the inside capillary, *d*, the glass is first thickened so that the final outside diameter at the tip will be 0.8 to 1.3 mm. and the inside diameter, 0.20 to 0.50 mm. The holder, *c*, is employed to keep *d* centered while the glass is worked. The weld is made at *g* until complete fusion has taken place and *a* is considerably thickened. The glass is then drawn out in the form, *e*, and cut at *f* where the outside diameter is 1.0 to 1.3 mm. and the inside diameter, 0.15 to 0.40 mm. It is highly desirable to have the delivery bore slightly smaller than the bore at *d*, so that the net capillary force of the filled pipet is in the direction of delivery. Otherwise drainage of the pipet into the adsorbent surface must be started with a gentle puff of air. The scratch at *f* may be made with a tungsten carbide crystal or a chip of porcelain, or by pressing the tube with a knife blade against a piece of silicon carbide paper and rotating. The inside diameter at *e* is 0.4 to 0.8 mm. and the length from inner tip to delivery tip is 25 to 40 mm. The over-all length is 130 to 150 mm. The delivery tip is beveled on emery polishing paper (Behr-Manning, Type O), so that the actual contact surface has a diameter of 0.5 to 0.6 mm. A plug of cotton batting is pushed into the shank of the pipet to protect the inner capillary tip from dust.

A pipet so made is completely automatic both in filling and in delivery into the chromatographic surface; neither suction nor

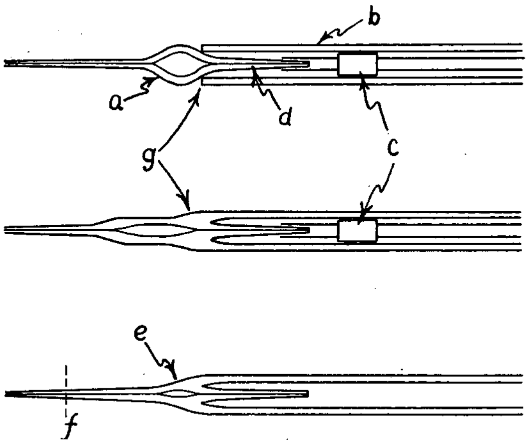

Figure 2. Construction of Sample Pipet

pressure is required. The technique consists of immersing the tip in the sample solution until the pipet is filled, removing and wiping off extraneous liquid with a filter paper, and resting the tip on the adsorbent surface until drainage is complete.

Another type of sample pipet may be prepared from a discarded thermometer stem. A delivery tip is drawn out having the dimensions given above. Because thermometers are often made of lead glass, it is advisable to use a reducing flame. Such a pipet has the advantage of giving a range of specified volumes, but automatic filling is sacrificed. The liquid is taken up above the desired mark, then adjusted to the mark by brushing the tip against a piece of filter paper. The liquid is then admitted into the adsorbent.

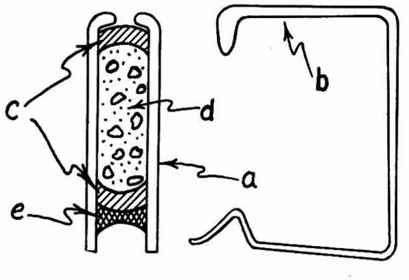

Figure 3. Absorbent Weighing Bottle

Calibration of these pipets may be accomplished by draining several pipetfuls of water into a wad of filter paper contained in a weighing bottle. For this purpose a convenient weighing bottle which guards against evaporation losses was constructed as shown in Figure 3.

It is made of 10-mm. glass tubing and at one end has a constricted opening, 2 mm. in diameter, for admitting the tip of the pipet. The over-all length of the tube, *a*, is 35 mm. Enclosed between two wads of filter paper, *c*, is a charge of anhydrous calcium sulfate (Drierite), *d*, the whole of which is secured by sealing wax, *e*. The glass spring-clip, *b*, fits into both ends and serves both as a stopper and as a carrying handle. Successive weighings of five pipetfuls each were found to vary by less than 0.1 mg.

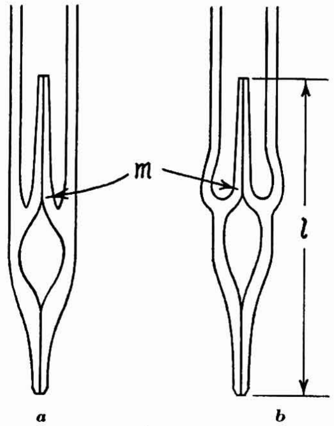

Figure 4. Developing Pipets

For use with adsorbent surfaces of approximately 0.5-mm. thickness, sample pipets of capacity 1 to 10 microliters (λ) have been found satisfactory. A typical thermometer stem pipet was found to have a capacity of 4.68λ when filled to the 100 mark and 3.03λ when filled to the 50 mark. This gives a volume increment of 0.033λ per division, assuming a uniform bore. Greater accuracy in calibration is possible but not required, for the accuracy of measurement of zone radii does not exceed three significant figures. Most R_f values appearing in the literature are recorded only to two significant figures.

A new type of developing pipet is shown in Figure 4.

This pipet is prepared in a manner similar to that employed for the sample pipet, Figure 2, except that a larger initial bulb is required. Both the inner capillary and the delivery capillary may be preformed; the final volume is adjusted by blowing after the weld has been made. *a* and *b*, Figure 4, are representative types of construction. The inner and outer capillary tips have the same dimensions as those given for the sample pipet. The length, *l*, is 35 to 50 mm.; the over-all length, 130 to 150 mm. For use with an adsorbent layer 0.5 mm. thick the delivered volume should be 40 to 70λ.

The calibration of this pipet is accomplished in the same manner as that used with the sample pipet, except that the weighing need be made only on a single pipetful. For this purpose a wad of filter paper at the bottom of an ordinary weighing bottle is adequate. The pipet may be filled by immersing the tip in the liquid and drawing it up into the bulb until it begins to enter the upper capillary at point *m*, Figure 4. At this point suction is discontinued and filling is completed by capillary action. An alternative method is to immerse the whole bulb below the surface of the liquid, in which case filling, though slow, is completely automatic. In routine work the authors have found it convenient to keep the pipet completely immersed in the developing solvent, inasmuch as the inner capillary is sufficiently small to retain the liquid even against a small hydrostatic head.

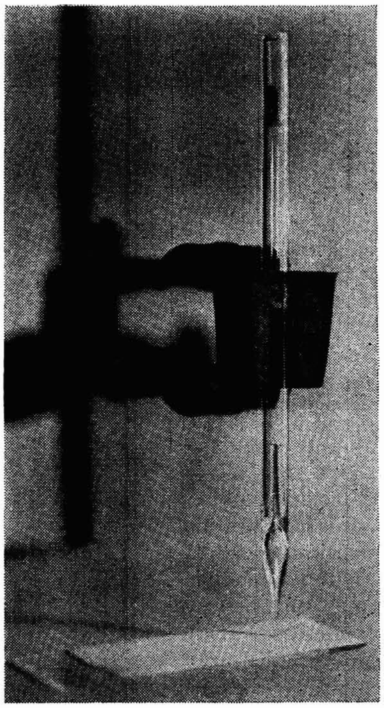

Figure 5. Developing Pipet and Support

In developing the chromatogram the filled pipet is applied at the same point as the sample and allowed to drain. Because development usually takes from 5 to 15 minutes, a support is necessary. In previous work (*3*) the support formed an integral part of the developing pipet. It has been found less cumbersome, however, to employ the system shown in Figure 5, in which a sectioned one-hole rubber stopper acts as a support.

The use of developing pipets of fixed volume makes possible the control of a previously troublesome variable: the volume ratio of developer to sample. This ratio, *Q*, is defined as

$$Q = \frac{\text{volume of developing solvent}}{\text{volume of sample}} \tag{1}$$

The value of *Q* in this sytem usually varies from 10 to 60. With a group of 16 sample pipets and 10 developing pipets, the authors obtained a series of *Q* values increasing gradually from 4.3 to 56.

A difficulty with this system when values of *Q* higher than 20 are employed lies in the necessity of making contact at exactly the same point with the developing pipet as was made with the sample pipet on the absorbent surface. If this condition is not fulfilled, the distribution of flow rates in the capillary channels of the adsorbent is upset and an irregular chromatogram results, the zone areas of which are difficult to measure except with a planimeter type of instrument.

This difficulty was circumvented by devising a slightly altered technique, using a pipet of the construction shown in Figure 6. The method of preparing this pipet follows the same procedure as that given above.

The length, l, is 90 to 115 mm., and the total volume is 50 to 75λ. In use the pipet is filled with both sample and developer, and the whole chromatrographic process is accomplished with a single application of the pipet to the adsorbent. The shank is graduated directly in values of Q, as indicated. The pipet is filled with water (or other developing solvent) to a point above the desired Q value; then the level is adjusted to the required mark by touching the tip to filter paper. The tip is freed of extraneous liquid and immersed in the sample solution, whereupon a volume of sample corresponding to the remainder of the inner capillary section is drawn in. The tip is again wiped off and applied directly to the adsorbent surface. The amount of water adhering to the inner walls after normal delivery was found to be, for a group of four pipets, 0.1 ± 0.05 mg. This introduces no error, particularly as the walls may be assumed to be uniformly wetted after each delivery.

Calibration is accomplished gravimetrically by obtaining the total contained mass of water and then calculating the mass required for a given value of Q. The pipet is filled in excess of this quantity, then adjusted to the required mass by careful drainage. The graduation thus obtained is marked with a tungsten carbide crystal.

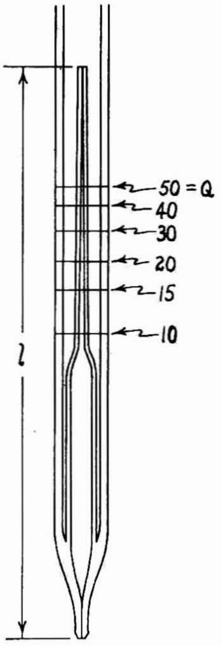

Figure 6. Combination Pipet

An obvious requirement in the use of this pipet is that the sample be made of sufficiently low pH to prevent hydrolytic precipitation of the cations by dilution at the developer-sample interface. This possibility is readily guarded against, because hydrogen ions diffuse much more rapidly than those metal ions which tend to form difficultly soluble hydrous oxides. The interface itself is small in area, and the pipet is applied to the adsorbent promptly after filling.

Pipet Support. The type of contact made by the tip of a pipet on the adsorbent surface has been found to be a critical factor in the formation of symmetrical chromatograms. Although the pipet holder shown in Figure 5 is conveniently arranged and gives fairly reliable results, an exactly reproducible angle of contact is not assured. Nonuniformities which are not readily apparent to the eye become obvious when radius measurements are taken. To obviate this difficulty the apparatus shown diagrammatically in Figure 7,*a*, was constructed. This system not only guarantees a vertical contact but also allows greater control in selecting the site of the chromatogram on the surface and in regulating the contact pressure. The contact pressure must be sufficient to embed the tip of the pipet somwhat in the surface, as shown in Figure 7,*b*. This is accomplished by lowering the pipet until it almost touches the surface and then giving the knurled knob a quick twist. If the pipet is lowered until contact between the tip and surface is just made, irregular capillary channels between the tip of the pipet and the surface will cause considerable distortion of the pattern. These channels are sealed off when the pipet is pressed into the adsorbent.

For much routine work and exploratory tests the support given in Figure 5 is adequate and obviously much simpler in design. The pipets illustrated in Figures 2 and 4 are likewise convenient where a large number of tests are to be made at one Q value. Their construction is simpler than the pipet given in Figure 6 and their operation is more automatic. On the other hand, the combination pipet and the improved support are to be preferred when a wide range of Q values is desired.

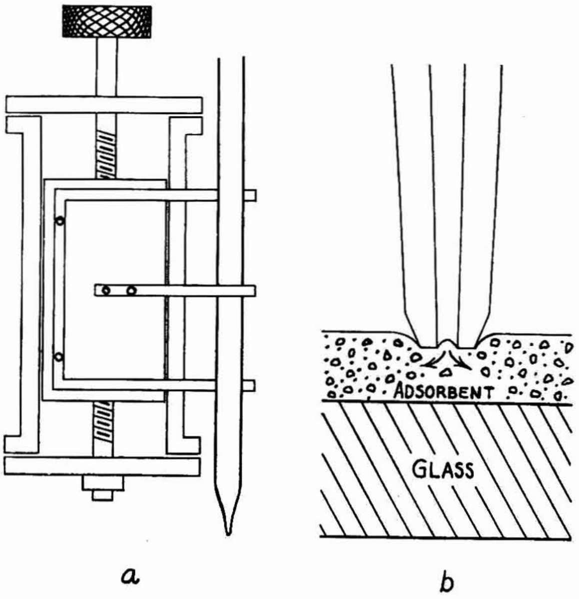

Figure 7. Controlled Application of Pipet to Adsorbent

Application of Reagents. An atomizer for applying reagents to a developed chromatogram is shown diagrammatically in Figure 8.

The device is conveniently blown from 7-mm. tubing and is mounted 18 to 20 cm. above the platform on which the slide is placed. Guides may be erected on the platform for the purpose of centering the chromatogram in the stream. The reagent is introduced from a dropper into the funnel at A and is drawn through the capillary by air pressure at B. Masks cut from sheet lead and placed on the chromatogram allow treatment of predetermined sectors, thus multiplying the number of reagents that can be applied to a single chromatogram. Although this enhances the qualitative possibilities of the technique, quantitative work requires uniform dye treatment if radius measurements are to be taken in all sectors.

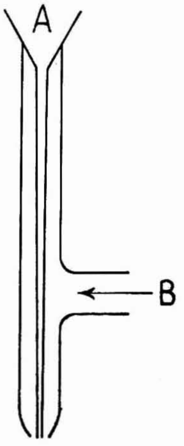

Figure 8. Atomizer

Radius-Measuring Devices. The use of a vernier caliper for radius measurements has been discarded as too tedious and inaccurate. Because as many as fifty chromatograms can be made conveniently in the course of a day using a single pipet of the combination type described above, and occasionally as many as ten sets of measurements are taken on a single chromatogram in order to obtain representative data, an expeditious method of measuring these radii becomes of paramount importance. A number of solutions to this problem have been tried, culminating in the following simple device.

A scale was ruled on a glass plate corresponding to Figure 9. This scale is calibrated in terms of radii but actually measures diameters. This was done to avoid using the center of the chromatogram as a reference point. Zone boundaries are considerably sharper than the indentation made by the developing pipet. Furthermore, an occasional chromatogram turns out to be fairly circular but slightly "off center," owing to inequalities in the surface at the point of contact of the pipet. In use the scale is placed face down on the chromatogram and its position is adjusted until a zone is tangent simultaneously to one of the parallel lines and the divergent line. The radius is read directly from the points of tangency. Each parallel line adds an increment of 2 mm. to the measurement as indicated on the scale at the bottom. This device was found to be decidedly more accurate and easy to use than the other instruments tested.

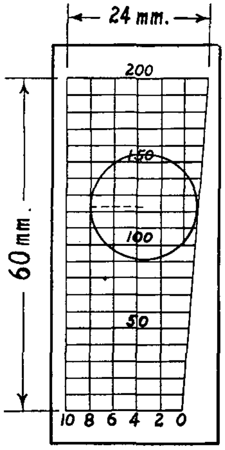

Figure 9. Transparent Scale

Mordant Dyes as Ripening Agents. The ripening of a developed chromatogram with iodine, and certain other specific reagents, has been discussed (*3*). It has been learned subsequently, however, that a tremendous range of highly selective reagents is available in the whole art of modern dyeing. The use of dyes offers the advantages of higher tinctorial powers, immediate insolubilization and immobilization of newly formed chromatographic zones, and extreme versatility in the selection of color contrasts for specific analytical problems. It was thought at first that developed dyes would best serve the purpose. Various reagents were atomized on the slide and diazo-coupled in situ to form the developed dye. Such treatment, however, resulted in "loading" of the adsorbent with liquids which tended to distort the yet unripened zones. A further inconvenience arose from the instability of stock solutions.

The best system for cation chromatography was found to be the direct application of mordant dyes. Such dyestuffs include a great number of the acid dyes, the alizarin dyes, anthracene and anthraquinone dyes, many of the chrome dyes, diamond blacks, browns, oranges, yellows, certain of the gallanil dyes, galleine, gallocyanine, rufigallol, certain of the sulfamines, and others.

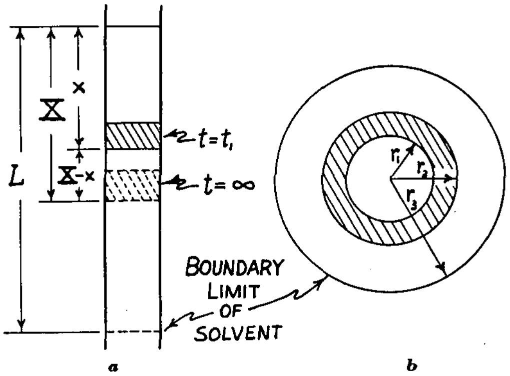

Figure 10. Chromatographic Zone Migration

The metal zones were found to be suitable mordants which formed intensely colored lakes upon application of the dye. Fixing of the zone occurs simultaneously, the resulting lake being insoluble and immobile. Qualitatively the method is particularly attractive because a single dye usually gives a range of different shades with different mordants. A dye mixture is even more versatile, because different mordants display marked dissimilarities in selectivity, and whereas one dye will displace another from a given mordant, it will not do so from another mordant. Although certain specific dye compositions are given herewith, a more general treatment covering over fifty alizarin and related dyes is being reserved for a later publication.

The following dye mixtures have been found useful in the detection and estimation of cobalt, nickel, copper, iron, and zirconium.

Dye Mixture I

National Superchrome Violet 2B (National Aniline and Chemical Company)	0.2%
Acid Chrome Green G (Fr. Bayer and Company, Germany)	0.3%

Dyestuffs dispersed in 0.1% Nacconol NR with gentle warming

Dye Mixture II

Acid Chrome Blue B (Fr. Bayer and Company)	0.3%
Alizarin Green V powder (Fr. Bayer and Company)	0.3%

Dyestuffs dispersed in 0.1% Nacconol NR with gentle warming

Dye Mixture III

National Alizarole Brown B (National Aniline and Chemical Company)	0.5%
Alizarin Yellow R (Coleman and Bell)	0.1%

Dyestuffs dispersed in 0.1% Nacconol NR with gentle warming

Dye Mixture IV

Sodium alizarin sulfonate (Merck)	0.3%

Dissolved in 0.02 *N* sodium hydroxide containing 0.1% Nacconol NR

Dye Mixture V

National Superchrome Violet 2B (National Aniline and Chemical Company)	0.50%
Acid Chrome Green G (Fr. Bayer and Company)	0.75%
Carbowax 4000 (Carbide and Carbon Chemicals Corporation)	2.0%

Ingredients dispersed in water with gentle warming

Of the first four compositions 6 to 8 drops are required in the ripening of a chromatogram 24 mm. in diameter. Only 2 to 3 drops of composition V are needed. The solutions are allowed to stand at room temperature a few days to allow separation of any solid materials. These compositions were found to be completely stable for indefinite periods. A dye-treated surface is allowed to dry, either by radiation from a heat lamp or at room temperature, and may then be spray-rinsed with a few drops of water. Rinsing often increases contrasts by carrying excess dye beneath the surface. A number of alternative procedures have been used with varying success.

THEORETICAL TREATMENT

Zone Migration. Qualitative detection of a metallic element may be accomplished not only by means of the lakes it forms with various dyestuffs but also by measuring its migrating characteristics in the chromatogram. The determination of these properties becomes possible when the quantity, Q (Equation 1), is fixed at definite values, and when the periphery, or boundary limit of the solvent, is readily visible. In the chromatography of protein hydrolyzates Consden and Martin have defined an exceedingly useful constant (*2*), the R_f value, which serves to identify amino acids and polypeptides in terms of their migrating characteristics. In such organic media, however, the possibility of precipitation of a zone to an immobile form ordinarily need not be reckoned with. A similar attack on the problem, which takes into consideration the limiting distance of migration, has been made in inorganic cation chromatography by Shemyakin and Mitselovskiĭ (*4*).

These investigators define a constant, k, by the equation

$$x = X(1 - e^{-kt}) \qquad (2)$$

the significance of which may be visualized by reference to Figure 10,*a*. The quantity, x, is the distance (millimeters) swept out by the front of the band during time t (minutes), and X is the limiting distance reached by the front of the band at equilibrium. The values of k for a selected group of cations were found to be reasonably constant for various values of t. A difficulty with this method of attack lies in the precipitation of a metal zone in the form of a hydrous oxide, or oxy-salt, which causes a decrease in effective pore size and a consequent restraint on the flow of developing solvent, and requires an applied pressure to maintain a constant flow rate.

These concepts may be profitably applied to radial surface chromatography. While the measurement of the developing time, t, is especially impractical in this system, a more direct and accurate value of the extent of development is found in the parameter, Q. The R_f value may be defined:

$$R_f = \frac{\text{movement of zone}}{\text{movement of solvent}} = \frac{x}{L} \text{ (Figure 10,}a\text{)} \qquad (3)$$

Table I. Chromatography of Nickel and Copper

	0.1 *M* Nickel Chloride in:					0.1 *M* $CuCl_2$ in 0.6 *N* HCl
	0.6 *N* HCl	0.4 *N* HCl	0.4 *N* HCl	0.6 *N* HCl	0.4 *N* HCl	
Q	1	2	3	4	5	6
	Values of ln r_3/r_2					
10	0.231 0.223	0.119 0.197	0.119 0.197	0.255 0.283	0.351 0.293	0.375 0.385
15	0.337 0.358	0.485 0.532	0.485 0.532	0.382 0.395	0.486 0.451	0.489 0.451
20	0.457 0.470	0.718 0.748	0.713 0.718	0.537 0.504	0.623 0.607	0.577 0.610
30	0.668 0.683	0.852 0.892	0.844 0.880	0.693 0.637	0.751 0.713	0.880 0.829
40	0.747 0.761	0.957 0.961	0.936 0.952	0.809 0.785	0.869 0.867	0.952 0.976
50	0.842 0.833	1.113 1.105	1.085 1.109	0.938 0.948	1.070 1.030	1.030 1.072
	Values of ln r_3/r_m where r_m is logarithmic mean of r_2 and r_1					
10	0.383 0.383	0.309 0.395	0.309 0.395	0.387 0.397	0.551 0.503	0.458 0.474
15	0.497 0.516	0.687 0.739	0.687 0.739	0.548 0.565	0.707 0.687	0.563 0.546
20	0.625 0.627	0.930 0.966	0.949 0.950	0.729 0.661	0.855 0.832	0.663 0.705
30	0.845 0.854	1.061 1.089	1.087 1.126	0.898 0.804	1.000 0.945	0.992 0.960
40	0.936 0.948	1.178 1.188	1.182 1.213	1.016 1.020	1.117 1.103	1.079 1.096
50	1.049 1.021	1.335 1.300	1.333 1.338	1.136 1.140	1.300 1.263	1.150 1.202

Assuming a constant surface depth throughout a given radial chromatogram, the volumes swept out by zone and solvent are proportional to the corresponding radii squared, and

$$R_f = \frac{r_2^2}{r_3^2} \text{ (Figure 10,}b\text{)} \qquad (4)$$

In the system under discussion, however, R_f is not constant but tends to approach zero as Q increases without limit—that is, r_2 approaches a limiting value as the cations are precipitated to a less mobile or immobile form. This may be accounted for by writing

$$a^2 \frac{r_2^2}{r_3^2} = e^{-kQ} \qquad (5)$$

in which a and k are constants.

For convenience k may be redefined as follows:

$$\frac{1}{2}\, k = M = \text{mobility function} \qquad (6)$$

The mobility function, M, is an expression of the rate of decrease in mobility of the metal zone with respect to the developer-sample volume ratio. Equation 5 then becomes:

$$a \frac{r_2}{r_3} = e^{-MQ} \qquad (7)$$

whence,

$$\ln \frac{r_3}{r_2} = MQ + \ln a \qquad (8)$$

The values of M and ln a are conveniently obtained by plotting ln r_3/r_2 against Q.

It should be noted that r_2/r_3 is not equivalent to $X - x/X$ (Equation 2), but to x/L. Furthermore, it is obvious that instead of r_2 alone, some mean value of the radii, r_1 and r_2, may be used. In the treatment of the data which follow, both the logarithmic mean of r_1 and r_2 and the leading edge alone, r_2, have been employed. These data have been selected to illustrate the mathematical treatment given here.

EXPERIMENTAL

Chromatography. The chromatographic process was carried out on microscope slides spread with layers of rigid adsorbent approximately 0.5 mm. thick, prepared according to the method described in an earlier publication (*3*). A single pipet of the combination type, graduated in Q values of 10, 15, 20, 30, 40, and 50, was used in all determinations. The developing solvent was water in every case, and was drawn into the pipet to the desired Q value prior to admitting the sample. The samples consisted of 0.1 molar nickel and copper chlorides in excess hydrochloric acid as specified in the column headings of Table I. The improved pipet holder described above was used in applying the pipet to the adsorbent. The slides used for the first three columns of data had been stored at room temperature and humidity; those used for the last three columns of data had been stored at room temperature and at a constant humidity of 81%.

Ripening. The chromatogram was allowed to air-dry until a wet spot was no longer visible on the underside of the slide (15 to 20 minutes, depending upon ambient temperature and humidity). Three drops of dye mixture V were then atomized on the slide, followed by 5 minutes' irradiation with a heat lamp. (This treatment corresponds to commercial mordant dye practice in which the treated fabric is usually immersed in a boiling dye solution.) Excess dye was then rinsed into the interior of the adsorbent by atomizing on the surface 6 drops of 2% Carbowax 4000 in water. Under these conditions the nickel is revealed as a pale blue-green zone; the copper, as a deep blue zone. The background color is pale violet; the central zone, red violet. The peripheral boundary of the solvent appears as a white ring.

It is possible to omit the rinsing process, in which case the peripheral boundary appears as a deep blue ring on a deep violet background. To test the effect of variations in dye treatment the data of column 2 (Table I) were taken on unrinsed chromatograms for Q values of 20, 30, 40, and 50. The data of column 3 are taken on these same patterns after rinsing.

Radius Measurements. All measurements were taken with the transparent scale described above. In taking these measurements it is convenient to inscribe diametric reference lines (dotted line, Figure 9) in various sectors of the surface with the aid of a thin-bladed steel spatula. Measurements are taken in those sectors which have the greatest uniformity of adsorbent depth. At the edges of the slide the adsorbent depth tapers off slightly, which may give rise to distortions in the chromatogram. Hence, those sectors lying longitudinally with respect to the slide are favored.

Table II. Duplicate Chromatograms of 0.1 *M* Nickel Chloride in 0.6 *N* Hydrochloric Acid

(Q = 10)

Radii, Cm.$^{-3}$					
r_1	r_2	r_3		ln r_3/r_2	ln r_3/r_m
553	757	954		0.232	0.385
559	762	962		0.232	0.385
567	771	975		0.235	0.385
564	771	965		0.224	0.377
			Av.	0.231	0.383
513	735	909		0.213	0.387
530	736	925		0.228	0.388
535	739	920		0.219	0.376
526	733	913		0.220	0.381
			Av.	0.220	0.383

A typical set of data is given in Table II. The practice has been to take several sets of radius measurements from a single chromatogram and to obtain from them an average value of the separately calculated values of ln r_3/r_2. It has been found more expeditious, however, to take only two sets of radius measurements and calculate the value of r_3/r_2 for each set. If these results deviate by less than 1.5%, no further measurements are taken. Larger deviations require additional sets of measurements in order to obtain a representative average. The data of the last four columns of Table I have been obtained by the latter method.

The data of Table I are plotted in Figures 11 to 14. With the exception of Figure 13, all curves are plotted on the basis of the outer zone radius rather than the logarithmic mean. The curves are numbered to correspond with the column numbers of Table I to which they refer.

DISCUSSION

The curves obtained from these data lend general support to the validity of Equation 7. The rate of decrease in mobility, M, of

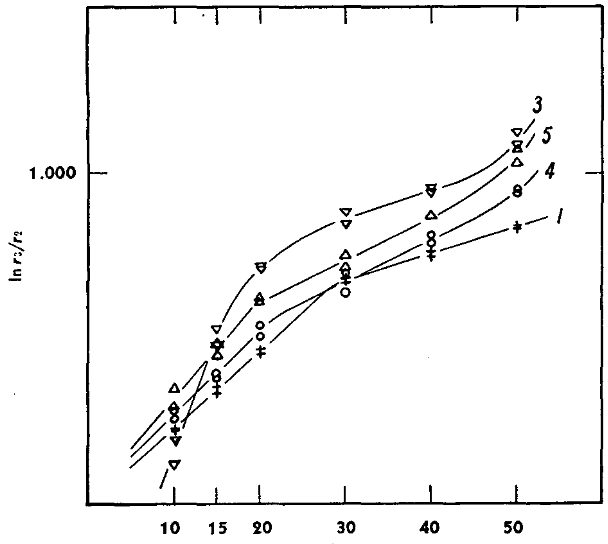

Figure 11. Chromatography of Nickel Chloride
Effect of humidity and acid concentration

the zone is found to be essentially constant during certain phases of the chromatographic development, giving rise to a linear relationship between ln r_3/r_2 and Q.

An approach to an interpretation of the chromatographic process may be made on the basis of these curves. Each curve is seen to have a more or less sharp point of inflection in the region, Q = 20 to 30, which is both preceded and followed by relatively linear segments. These points of inflection represent a change in the rate of decrease in the mobility of the zone being measured and indicate an alteration in the chemical processes taking place within it. Thus, the first segments (Figure 11) are due to the migration of nickel chloride and an excess of hydrochloric acid; the second segments arise from nickel chloride alone—that is, hydrochloric acid is adsorbed first and occupies the center of the chromatogram. This effect is evident from the chromatographic pattern itself, and from the chromatography of pure hydrochloric acid alone. It is also evident from the fact that the point of inflection is shifted to the left (curves 4 and 5) when the concentration of hydrochloric acid in the sample is decreased.

The significance of the mobility function, M, may also be understood on this basis. When an excess of hydrochloric acid is present, the rate of decrease in mobility is greater, owing to the rapid adsorption of the excess acid. At the breaking point in the curve the mobilizing effect of the acid vanishes, and the rate of decrease in mobility becomes that characteristic of nickel chloride alone. This decrease in mobility is due to the gradual hydrolysis of nickel chloride to an immobile species. Extrapolation of the second part of the curve to the ordinate gives ln a for that portion of the curve, and predicts the progress of immobilization of nickel chloride if no excess acid had been added to the original sample. Also in this portion immediately following the point of inflection hydrochloric acid is being extracted from the central portion of the chromatogram by fresh solvent. Thus, the adsorption of hydrochloric acid arising from hydrolysis of the nickel chloride is partially balanced by this additional acid, and a steady state is maintained for a short interval. In certain cases the rate of immobilization begins to increase rapidly in the region, Q = 50. This is regarded as evidence that precipitation to a completely immobile product is beginning to take place.

The value of the constant, a, which is the reciprocal of the mobility of the zone at Q = 0, should be characteristic of the individual metal under specified conditions, and should be independent of the presence of varying amounts of other ions—e.g., hydrogen ion—which do not alter the process in a fundamental manner. Although present data suggest this possibility in specific instances, they cannot be regarded as proof in the absence of a more extended survey.

Certain comparisons of interest, however, may be drawn with confidence. Curves 4 and 5 (Figure 11) show the effect of hydrochloric acid concentration on a sample of 0.1 molar nickel chloride. For curve 4 the samples were 0.6 N in hydrochloric acid; for curve 5, 0.4 N. Immediately obvious is the fact that in 4 the zone is more mobile than in 5, inasmuch as curve 5 lies above curve 4. The acid is adsorbed more rapidly and the mobility of the zone decreases more sharply for the lower acid concentration, as indicated by the steeper slope of the first segment of curve 5 and the shift in the point of inflection. The adsorption of hydrochloric acid is believed to be dependent not only on the available surface area of the alumina, but also on the coating of these particles with a starch binder, the starch acting as an adsorbent for the strongly hydrophilic hydrogen ion. It is apparent, both from the chromatographic sequence and from the curve, that nickel ion displays less tendency to associate with the adsorbent than does hydrogen ion.

This view finds further support in an examination of the effect of humidity on the adsorbent. Curves 4 and 5 were taken on slides stored at 81% humidity (room temperature). Because the swelling of starch by atmospheric moisture requires a finite period of time, and the chromatographic process is complete in 5 to 10 minutes, no significant changes in the structure of the adsorbent take place during development under conditions of uncontrolled humidity (ambient humidity). Slides which are stored at ambient humidity, however, show marked differences in behavior toward the migration of a zone, as indicated by curves 1 and 3 (Figure 11). Curve 1 is a duplicate of curve 4; curve 3 is a duplicate of curve 5. In the case of curve 1 the ambient humidity was below 81%; in the case of curve 3 it was greater than 81%.

By comparing curve 1 with curve 4 it is evident that at lower humidities the excess acid is adsorbed less rapidly and the over-all mobility of the nickel zone is greater and apparently still linear through Q = 50. Conversely, by comparing curve 3 with curve 5, it appears that increased humidities result in much more rapid adsorption of hydrochloric acid and a much greater restraining effect on the migration of the nickel zone. These facts may be regarded as further evidence of the swelling of the starch as a controlling factor in this process. The swelling of the starch reduces the effective pore size and tends to inhibit zone migration. It also offers, presumably, a greater array of hydroxyl groups which more readily adsorbs the excess hydrochloric acid.

It will also be seen from a comparison of these curves that increasing humidity is accompanied by a greater deviation in duplicate chromatograms and by a greater departure from linearity. All these facts point to the importance of accurately controlling both the starch content of the surface and the storage humidity. Furthermore, they suggest a useful means of varying the surface characteristics to suit the needs of a specific analytical problem. The chromatography of copper chloride, for example, is so hindered at a storage humidity of 81% that a developing period of 10 to 15 minutes is attained only by constant readjustment of the pipet pressure against the surface. Because solvent evaporation takes place during development, long developing periods must be avoided. Copper chloride is easily chromatographed at lower adsorbent humidities.

Curves 4 and 6 (Figure 12) describe the chromatography of 0.6 N hydrochloric acid solutions of 0.1 molar nickel and copper chlorides, respectively. The data were taken on slides humidified at 81%. It is obvious from the relative positions of the curves that copper is less mobile than nickel. This fact is borne out experimentally when copper and nickel are chromatographed together; the copper zone follows the nickel zone. The vertical distance between the two curves at any given value of Q gives a Δln r_3/r_2 which characterizes the difference in mobilities of the two metals at that point. When a number of metals are to be chromatographed at the same time, it should be possible, by a comparison of the individual curves, to pick that Q value which would most enhance the separation of a given pair among them.

Both the position and shape of the curves appear to be characteristic of the elements. Because copper chloride hydrolyzes more readily in water than does the nickel salt, hydrochloric acid is yielded to the environment over a longer period in the initial stages of the development of the copper. The shift to the right of the breaking point in the copper curve (curve 6) is regarded as evidence of this fact. Other factors, however, such as the association between the copper and the adsorbent and the character of the copper hydrolyzate, may also contribute to the location of the point of inflection. It seems likely that such curves may serve as a useful means of qualitative identification of an element, especially by juxtaposing the chromatography of a known element.

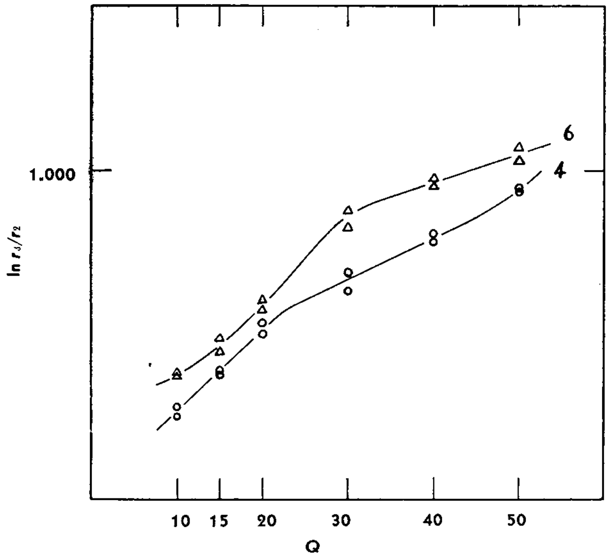

Figure 12. Chromatography of Copper (6) and Nickel (4) Chlorides

The linearity of these curves, especially at lower humidities, suggests the existence of a constant pH gradient in the chromatogram. If this is true, the position of the breaking point in the curve should give information concerning the stability of the metal salt involved and its solubility product constant, but data are as yet insufficient to decide this point.

Although the data presented here are calculated on the basis of both the leading edge radius and the logarithmic mean radius of the metal zone (Table I), the differences in the plotted curves have been found insufficient to warrant reproduction of all of them. A typical comparison is given in Figure 13, which describes the chromatography of 0.1 molar nickel chloride in 0.4 N hydrochloric acid. While the upper curve is characteristic of the zone as a whole, its general shape varies little from the curve obtained from ln r_3/r_2. The vertical distance between the two curves gives information concerning the depth of the zone, but for this purpose a plot of ln r_3/r_1 would, perhaps, serve better. In most cases the use of the logarithmic mean radius gives somewhat smaller deviations between duplicate chromatograms, and between sets of radius measurements taken from different portions of a single chromatogram, than does the use of the leading edge radius alone. This effect is not large enough with present data to demand exclusive use of the logarithmic mean radius, especially when one considers the relatively greater ease of calculation using the leading edge only.

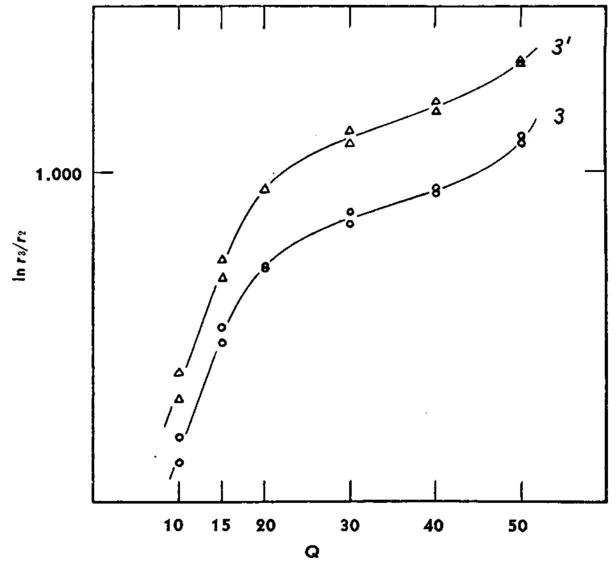

Figure 13. Logarithmic Mean (3′) *vs.* Leading Edge (3)

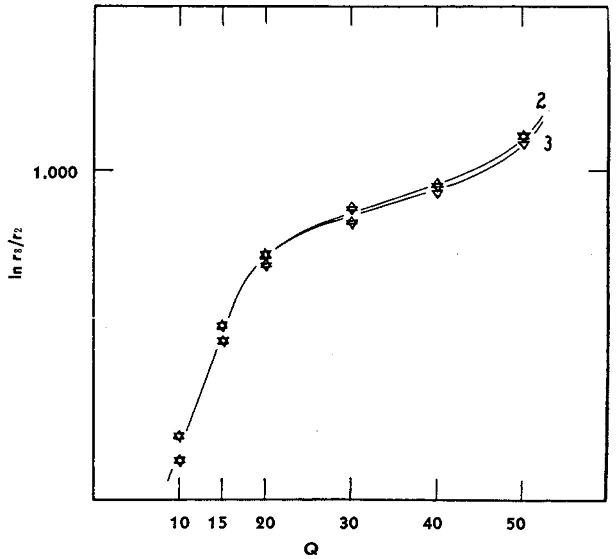

Figure 14. Effect of Alterations in Ripening Process

2. Rinsing omitted

The value of M increases more rapidly in the region, $Q = 50$, with the leading edge of the zone (curve 3) than with the logarithmic mean radius (curve 3′). This "compression" of the zone has been noted in other cases, and is interpreted to indicate precipitation of hydrous metal oxide at the outer edge due to the continued increase in pH.

Figure 14 demonstrates the effect of alterations in dye treatment (ripening). In curve 2 a rinsing operation has been omitted, as described earlier. Measurements for both curves were taken on the same patterns, using the same reference lines. Although changes in the amounts of reagents atomized on the surface have a negligible effect on measurements, alterations in the procedure which result in different types of color contrasts (such as the omission of a rinsing, or the use of a different dyestuff) will cause significant changes.

The data of Table I also give information concerning variations in depth of adsorbent surface. No convenient means has yet been devised for ensuring a constant and uniform surface depth in the preparation of the slides (*3*). It has been the opinion of the authors, however, that small variations in surface depth from one slide to the next would not alter the radius ratios even though the radius measurements themselves varied by as much as 1 mm. or more. This assumption is validated in the data of columns 4 and 5, where all duplicate chromatograms were made on separate slides. No significant increase in deviation between duplicates has been noted. Although a more uniform surface depth would be desirable, it may be concluded that the present surfaces are adequate for preliminary studies.

The material presented herein admittedly leaves many questions unanswered. Perhaps most desirable would be a correlation between the chromatographic behavior curves of single elements and the degree of their separation from mixtures. The effect of varying amounts of an impurity on the curve of a given element would be useful. The use of developing solvents other than water, such as dilute hydrochloric acid, has been examined but no organized study made. A number of other problems suggest themselves. The complexing effect, for example, of various anions on a given cation might be studied. Because complexing reduces the hydrogen ion concentration available to the adsorbent, this effect should be measurable by a shift in the point of inflection of the curve. It is hoped that the present study will evoke interest in some of these problems.

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Magnesium Content of Plant Tissue

Microchemical Determination through Thiazole Yellow Procedure

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A procedure is proposed for rapid and accurate microdetermination of the magnesium content of plant tissue, without removal of other ions or addition of compensative solutions. The prescribed nitric acid–perchloric acid solution of plant tissue is also utilizable for the determination of the concomitant content of calcium, potassium, sodium, and phosphorus, and also nitrogen content in a solution of plant tissue obtained by means of the alternative sulfuric acid and selenium oxychloride digestion (*5*).

IN A comparison of 130 organic compounds as reagents for the determination of the magnesium content of soil extracts, Mikkelsen and Toth (*6*) found thiazole yellow (sodium 2,2-disulfonate of methylbenzothiazole) to be the best by far. In two subsequent investigations at the New Jersey Station, thiazole yellow was utilized in a macroprocedure for the spectrophotometric determination of the magnesium content of solutions that had been freed of interfering ions by means of sodium tungstate and sodium phosphate (*3*, *7*, *8*) or the removal of calcium and R_2O_3 by the A.O.A.C. method (*1*).

Because it appeared more advantageous than the official method, the cited procedure was studied in an effort to adapt it to the microdetermination of the magnesium content of plant tissue. The procedure that has proved acceptable in the use of 2-gram charges of plant tissue (*2*, *7*, *8*) was found infeasible for the microanalysis of a solution derived from a charge of only 0.2 gram of plant tissue.

Further study demonstrated that the thiazole procedure could be simplified and adapted to routine microdeterminations of the magnesium content of plant material and without necessity for the prior removal of calcium, manganese, iron, and aluminum from the solution of a 0.2-gram charge of plant tissue. The resultant microprocedure for magnesium was checked thoroughly against the official method (*1*) and found to give accurate results, while also affording a single solution for determinations of the companion elements.

ADAPTATION OF THIAZOLE YELLOW TO PROPOSED MICROCHEMICAL PROCEDURE

Mikkelsen *et al.* (*7*) prescribed that a 2-gram charge of plant material be brought into nitric-perchloric acid solution for the determination of magnesium by means of thiazole yellow. Because that charge is too large for use in routine microchemical analysis, small aliquots of the solutions derived through digestions of only 0.2 gram of plant material were used for the microchemical determination of magnesium. (The remaining portion of this solution can be used for the microchemical determination of phosphorus, calcium, and potassium.) These trials proved disappointing, however, because the adjustment of the pH of each solution in order to effect the prior removal of calcium, manganese, iron, and aluminum as tungstates militated against speedy analyses. Further work served to establish the fact that adjustment of the pH values and prior removal of the cited elements are not necessary for accurate and rapid microdeterminations of magnesium through the use of aliquots of the solution derived from a 0.2-gram charge. When a small aliquot of such a solution is evaporated to dryness on an electric plate and then calcined in a muffle furnace, the residue can be dissolved and the color then developed with the addition of the respective reagents, with results concordant to those obtained by means of the official method.

TESTING THE REAGENTS

In the course of this study, each reagent was tested in aliquots larger or smaller than those of Mikkelsen *et al.* (*6*) to ascertain whether the color intensity and persistence of the solutions could be improved in the analytical procedure. The reagents behaved in the manner noted by the cited investigators, with the exception of the starch solution. When that reagent was compared with a 3% solution of gum acacia, and with a 0.5% solution of gum ghatti, the gum ghatti reagent was found more suitable for use

Table I. Noneffect of Calcium on Determination of Magnesium Content of Plants

(Thiazole yellow micromethod)

Calcium Additions	Total Calcium Present		Magnesium Recovery	
Mg.	*Mg.*	%	*Mg.*	%
None	2.42	1.21	0.96	100
0.5	2.92	1.46	0.96	100
1.0	3.42	1.71	0.92	96
1.5	3.92	1.96	1.02	106
2.0	4.42	2.21	0.90	94
2.5	4.92	2.46	0.94	98

with either filter 540 in the Evelyn photoelectric colorimeter or filter 525 in the Fisher electrophotometer.

NONEFFECT OF CALCIUM IONS IN THE MICROANALYSES

Evidence that coincidence of calcium solutes does not affect the microdetermination of magnesium by means of the thiazole yellow method was noted first in the findings given in Table I, wherein no provision was made for prior removal of calcium content. The possibility of calcium interference in microanalyses was tested further by the use of multiple charges of 0.2 gram of red clover, fortified by calcium additions of 0.5, 1.0, 2.0, and 2.5 mg. in the form of calcium chloride, as stipulated in Table II. Because the clover had a calcium content of 1.21%, the additions brought the calcium contents in the range between 1.21 and 2.46%.

Table II. Recovery of Magnesium from Additions to Standard Red Clover by Proposed Microchemical Procedure

Magnesium Additions	Total Magnesium Present	Total Magnesium Found	Recovery of Additive Magnesium
Mg.	*Mg.*	*Mg.*	%
None	0.96	0.96	...
0.5	1.46	1.50	103
1.0	1.98	1.98	101
1.5	2.46	2.52	102
2.0	2.96	3.02	102
2.5	3.46	3.44	99

The fortified charges were digested as usual and the magnesium contents of the resultant solutions were determined colorimetrically by the thiazole yellow micromethod. The findings presented in Table II show noninterference from calcium, when present in proportions that might occur in tissue of calciphiles.

EFFECT OF MANGANESE, IRON, AND ALUMINUM IN MICROANALYSES OF PLANTS

Although the natural occurrences of manganese, iron, and aluminum had given no evidence of interference in the microdetermination of magnesium in previous experiments, the possibility of such interference was explored through separate additions of those three elements in 0.2-gram charges of red clover, as in the case of additive calcium. The amounts of each element added were: 0.02, 0.04, 0.08, 0.12, 0.16, 0.20, 0.24, and 0.30 mg., as manganese sulfate, ferrous sulfate, and aluminum chloride. Those additions were equivalent to 0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, and 0.15% of each element. Total percentage occurrences are not given in the presentation of findings in Table III, because the amounts of the three elements naturally present in the clover were not determined.

The analytical findings presented in Table II show that manganese and iron did not interfere in the determination of magnesium, when occurrences of each of those two elements in the plant materials were not higher than 0.15%, and aluminum was not higher than 0.08% in air-dried material. The experimentally imposed percentages of the three elements are beyond those to be expected in normal calciphiles and, therefore, the small amounts natural to plant material did not interfere in the microdetermination of magnesium (*2*).

ADAPTABILITY OF THIAZOLE YELLOW PROCEDURE TO MICROCHEMICAL TECHNIQUE

In the course of this study, it was observed that the color of the solution changes gradually, although not to the extent of serious vitiation of the results. This disadvantage can be obviated, however, through the preparation of a fresh standard tinted solution for the calibration curve in each set of determinations. The reading obtained from the calibration curve then will be more accurate, because the change in the tint of the "unknown" is likely to occur in parallel with the change in the tint of the standards, from which the calibration curve is constructed.

It is advantageous also to have a systematic arrangement of the steps in the analytical procedure. After the last reagent is added to develop the tint in the unknown solution and in the standards, the solutions should be made to volume and the colorimetric reading should be taken immediately, so that any error resultant from the effect of light upon the solutions is diminished to a minimum.

Presence of perchloric acid in the solutions tends to induce gradual fading of the tint or its failure to develop. Perchloric acid fumes are likely to adhere on the sides of the beaker during evaporation and they should be expelled. Their complete removal after evaporation is accomplished by placing the beaker in muffle furnace for 15 to 20 minutes at 550° C.

PREPARATION OF REAGENTS

Nitric acid, concentrated.

Perchloric acid, 70 to 72%.

Hydrochloric acid, 1 + 1.

Hydroxylamine hydrochloride, 5%. Dissolve 5 grams in a 100-ml. flask, make to volume, filter, and store in a glass-stoppered bottle.

Sodium hydroxide, 3 *N*. Transfer 162 ml. of 1 + 1 stock solution of sodium hydroxide into a 1000-ml. volumetric flask, add 600 ml. of water, shake, and cool. Make to volume, and transfer to a reagent bottle. No standardization is required.

Thiazole yellow solution. Dissolve 0.25 gram of thiazole yellow in 500 ml. of water and store the solution in an amber glass-stoppered bottle.

Gum ghatti solution, 0.5%. Put 200 ml. of water in a 400-ml. beaker and add 1 gram of powered gum ghatti, while stirring to effect complete dissolution without caking. Centrifuge the solution, filter the supernatant through a fluted filter, transfer the filtrate into a reagent bottle, and store it in the refrigerator.

Table III. Effect of Coincidental Occurrences of Manganese, Iron, and Aluminum on Determination of Magnesium Content of Plant Solutions

(Thiazole yellow micromethod)

Elements Added		With Manganese Additions		With Iron Additions		With Aluminum Additions	
		Magnesium found	Recovery	Magnesium found	Recovery	Magnesium found	Recovery
Mg.	%[a]	*Mg.*	%	*Mg.*	%	*Mg.*	%
None	..	0.96	100	0.96	100	0.96	100
0.02	0.01	0.96	100	1.00	104	1.00	104
0.04	0.02	1.02	105	1.00	104	0.98	102
0.08	0.04	0.92	96	0.98	102	0.96	100
0.12	0.06	1.04	108	0.98	102	0.96	100
0.16	0.08	1.00	104	0.98	102	0.88	92
0.20	0.10	1.02	106	1.02	106	0.84	88
0.24	0.12	0.96	100	1.04	108	0.84	88
0.30	0.15	0.96	100	0.96	100	0.98	102

[a] Basis of air-dry material.

Standard Magnesium Sulfate Solution. Solution A, 1 ml. = 1.0 mg. of magnesium. Dissolve approximately 12 grams of C.P. magnesium sulfate ($MgSO_4.7H_2O$) in a 1000-ml. volumetric flask and make to volume. Introduce 10-ml. aliquots into beakers, determine magnesium by means of the official method (*1*), and use the results in adjustment of solution A, so that 1 ml. will contain 1.0 mg. of magnesium.

Solution B. Transfer 20 ml. of solution A into a 1000-ml.

volumetric flask and make to volume, so that 1 ml. will contain 0.02 mg. of magnesium.

PROCEDURE

Weigh 0.2 gram of finely ground plant material into a 50-ml. beaker, saturate the charge with 2 ml. of nitric acid, and then add 3 ml. of perchloric acid. Cover the beaker with a watch glass and rotate the beaker to effect a thorough mixing of its contents. Place the beaker on a cold plate topped with asbestos cloth to afford gradual and uniform distribution of applied heat. Raise the temperature of the plate gradually until the solution becomes clear. Hold the beaker by means of tongs and rotate the liquid to facilitate oxidation of any organic matter that may have adhered to the sides of the beaker. Return the beaker to the plate and digest to evolution of fumes, but not to dryness.

Table IV. Determination of Magnesium Content of Plants

Sample No.	Plant Material[a]	Official Method[b] %	Thiazole Yellow Micro-method[c] %
83-1	Rye grass	0.57	0.59
97-1	Rye grass	0.34	0.35
99-1	Rye grass	0.50	0.51
103-1	Rye grass	0.39	0.38
111-1	Red clover	0.68	0.71
125-1	Red clover	0.50	0.53
127-1	Red clover	0.68	0.69
131-1	Red clover	0.51	0.54
83-2	Rye grass	0.57	0.60
97-2	Rye grass	0.38	0.42
99-2	Rye grass	0.63	0.65
103-2	Rye grass	0.47	0.47
111-2	Red clover	0.60	0.65
125-2	Red clover	0.43	0.45
127-2	Red clover	0.73	0.76
131-2	Red clover	0.51	0.50
241-2	Sudan grass	1.11	1.16
251-2	Sudan grass	0.97	1.02
259-2	Sudan grass	0.23	0.24
273-2	Sudan grass	0.77	0.82
281-2	Sudan grass	0.38	0.37
285-2	Sudan grass	0.38	0.38
293-2	Sudan grass	0.70	0.72
Standard	Clover	0.48	0.48
Av.		0.56	0.58

[a] Plant materials from pot cultures of soils variously fertilized with or without liming.
[b] Gravimetric.
[c] Colorimetric.

Cool, rinse the watch glass coatings into the beaker, transfer the solution into a 100-ml. flask, make to volume, and let stand overnight. Transfer 10 ml. of the clear supernatant solution (remaining portion of this solution can be used for the microchemical determination of phosphorus, calcium, and potassium) into a 50-ml. beaker and evaporate to dryness. Place the beaker in a muffle furnace 15 to 20 minutes at 550° C. Cool, rinse the beaker, add 2 drops of hydrochloric acid (1 + 1) to dissolve the residue, and transfer into a 50-ml. flask, holding the solution to 25 to 30 ml. Add 2 ml. of the gum ghatti solution, 1 ml. of hydroxylamine, 1 ml. of thiazole yellow, and 1 ml. of sodium hydroxide, agitating the solution thoroughly after addition of each of the reagents in the order given. Make to volume and shake vigorously. Transfer 15 to 20 ml. into an absorption tube and take transmittance reading with a photoelectric colorimeter, by means of either filter 540 of the Evelyn photoelectric colorimeter or filter 525 of the Fisher electrophotometer.

For each series of determinations prepare standards to contain 0.0, 0.02, 0.04, 0.06, 0.10, 0.14, and 0.20 mg. of magnesium through use of magnesium sulfate solution B and then follow the procedure outlined above, beginning with the prescribed addition "add 2 drops of hydrochloric acid (1 + 1)." Make a calibration curve from the transmittance readings, and compute the values for the unknown as per cent of magnesium content of the plant material.

ACCURACY OF DETERMINATION OF MAGNESIUM BY PROPOSED PROCEDURE

The accuracy of the thiazole yellow micromethod was verified through the further comparisons of Table IV. The 24 samples of rye grass, red clover, and Sudan grass were analyzed for magnesium content by means of the official gravimetric method (*1*) on 1-gram charges of the several plant materials and by the use of 10-ml. aliquots of 0.2-gram digestates in the analyses obtained by means of the proposed microprocedure. The findings presented in Table IV show that the thiazole yellow procedure can be used effectively for the microchemical colorimetric determination of the magnesium content of plant materials.

Because of the necessity of determining magnesium in large numbers of lysimeter leachings and rain waters, an attempt was made to adapt the prescribed microprocedure to the analysis of those solutions. It was found, however, that the microdetermination by means of the yellow thiazole reagent could not be made with accuracy, without prior elimination of calcium and R_2O_3 either through the step prescribed by Toth *et al.* (*8*) in the use of the microprocedure, or through the addition of the "starch-compensating" solution prescribed by Drosdoff and Nearpass (*4*) in the use of 1-ml. aliquots of 100-ml. digestates of 2-gram charges of tung leaves for colorimetric analyses.

SUMMARY

In an attempt to adapt the thiazole yellow method to a microchemical procedure for the determination of the magnesium content of solutions of plant tissue, it was found that the prior removal of calcium, manganese, iron, and aluminum is unnecessary. There was no interference by these elements in the small aliquots of the digestates derived from a 0.2-gram charge of plant tissue. Certain modifications then were introduced to render the thiazole yellow method suitable for the microchemical determination of the magnesium present in plant tissue.

The findings obtained by the proposed microchemical procedure were in satisfactory agreement with the results obtained through the use of the A.O.A.C. official method.

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Polarographic Determination of Folic Acid—Correction

Louis and Thelma Meites have called attention to the following corrections that should be made in the article entitled "Polarographic Determination of Folic Acid" [Anal. Chem., **20**, 1199 (1948)].

The weight of reagent cadmium chloride used per liter should be 115 mg. and not 115 grams. A negative sign should appear before the voltages expressed in the text and in Figure 1. Figures 1 and 2 are transposed.

In accordance with a suggestion of the Meites, the authors have investigated a supporting electrolyte containing an equivalent amount of ammonia in lieu of the tetramethyl ammonium ion and have obtained similar polarograms with both solutions.

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Kjeldahl Method for Total Nitrogen

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The most important unsolved problems of the Kjeldahl method for total nitrogen are concerned with digestion conditions. The quantity of sulfuric acid used in comparison to the size of sample, and the amount of added salt, are factors of importance. Addition of extra sulfuric acid during digestion is often desirable. Mercury is the most effective catalyst for digestion of proteins and usually cannot be satisfactorily replaced by selenium, which must be kept under constant control. Oxidizing agents, except hydrogen peroxide, should be used only with the greatest care. Length of digestion after clearing requires further attention. The milligram scale Kjeldahl method is recommended for general application. The ultramicromethod, in which the ammonia is separated by diffusion, is convenient and suitable for many small scale uses. Significant developments in reducing the size of sample into the submicrogram range are to be expected, through use of the spectrophotometer equipped with capillary cells, and improvements in spectrophotometric instrumentation.

MANY discoveries of far-reaching importance have been fundamentally extremely simple. The discovery that boiling many nitrogen-containing organic compounds in concentrated sulfuric acid liberates the nitrogen in the form of ammonium sulfate is probably one of the most significant analytical discoveries ever made. Attributed to Kjeldahl, who announced the method in 1883, this method has probably been applied in one modification or another to every possible form of nitrogen, and in perhaps more laboratories than almost any other single type of analytical method.

The method was first developed for and applied to the analysis of protein nitrogen, and in the analysis of this material some of the greatest difficulties inherent in the method are still only partially solved. Within the past 5 years, papers by Chibnall, Rees, and Williams (*5*), Jonnard (*11*), and others have emphasized the difficulties of obtaining quantitative recovery of the nitrogen from proteins by the Kjeldahl method. Perhaps it is more surprising that merely cooking one of the most refractory and difficultly manipulated biological materials with concentrated sulfuric acid could be made to yield dependable results than that it fails at times to recover all of the nitrogen. In spite of the lapse of 65 years since the inception of the method, and the hundreds of papers published on its use, there is little accurate information on the nature of the breakdown taking place in the Kjeldahl digestion when different compounds are treated with hot sulfuric acid, and on the reactions, their mechanisms, or their rates. Hundreds of empirical studies on the effects of catalysts, oxidizing agents, added salts or other acids, and time and conditions of digestion have been published. Few if any accurate studies have been made on the intermediate chemistry of the digestion.

Bradstreet (*2*) in 1940 extensively reviewed the subject of Kjeldahl analysis, quoting 148 references, most of which were empirical studies of the effects of alteration in digestion combinations. More recently, the application of the Kjeldahl method to the analysis of protein nitrogen was reviewed by Kirk (*13*), who listed approximately 90 references, most of which were also concerned with similar empirical studies.

All Kjeldahl digestions are subject to four simple facts:

1. Sulfuric acid is a very weak oxidant, which would not be expected to oxidize organic materials rapidly.
2. The conditions existing in the Kjeldahl digestion are essentially favorable to reduction, as indicated by the fact that the ammonia is not oxidized to nitrogen, and that oxidized forms of nitrogen may be partly or wholly reduced during digestion, almost entirely by organic residues undergoing decomposition.
3. The high temperature of the digestion is conducive to pyrolytic decomposition of many compounds.
4. Because of the rapid removal of water-forming groups by the hot sulfuric acid, charring will always tend to occur.

The fact that the necessary conditions for reduction of nitrogen must coexist with oxidizing conditions for the remainder of the decomposed organic molecules gives an indication of the narrow oxidation-reduction range in which the decomposition must be carried out. Disregard for this fact has led to numerous unsatisfactory modifications in which strong oxidizing agents were used or other conditions were modified unfavorably.

Any discussion of the Kjeldahl method must be divided logically into consideration of the digestion, the separation of ammonia (or its omission), and the determination of ammonia. Except as applied to microchemical or other special techniques, the separation and determination of ammonia may be carried out by a number of very satisfactory procedures which are chosen almost solely on the basis of their rapidity, simplicity, or the personal preference of the analyst, rather than on any fundamental chemical basis. The digestion, on the other hand, which has been most investigated, also calls most imperatively for further fundamental and thorough study. It is indeed probable, as indicated by the extensive work of Friedrich, Kuhaas, and Schnurch (*9*), that no single digestion method of universal application will ever be found, but rather that the details of the digestion technique and conditions will have to be determined very largely by the nature of the material digested. This paper does not review in detail the modifications of digestion and the studies made upon them, but it summarizes the most important generalizations that can be made on the basis of the large number of empirical studies that are available.

DIGESTION CONDITIONS

Amount of Sulfuric Acid Used. This question is related to the amount of potassium sulfate or other salt added to raise the boiling point. At no time must the composition of the mixture approach that of potassium acid sulfate, or ammonia will be lost, in fact, almost quantitatively at the composition of potassium acid sulfate. This question was investigated extensively by Self (*28*), who states that a 15-gram excess of sulfuric acid should remain if 25 ml. were used initially with 10 grams of potassium sulfate. Inasmuch as the utilization of sulfuric acid varies from 7.3 grams for 1 gram of carbohydrate to 17.8 grams for 1 gram of fat, and 6.7 grams of the acid go to the formation of acid sulfate with 10 grams of potassium sulfate, extra sulfuric acid should often be added in the middle of the digestion, particularly when the latter is long continued, as is frequently recommended for protein analysis. This conclusion is confirmed by various investigators.

Amount and Kind of Added Salt. The addition of neutral salt to raise the boiling point, first introduced by Gunning (*10*) in 1899, is effective in increasing the rate of digestion and is almost universally used. It can lead to the loss of very significant quantities of ammonia when used in too great excess, or when the amount of sulfuric acid is allowed to diminish. In the Kjeldahl micromethod particularly, the use of added salts has been less common, and the amounts are smaller in proportion to the macromethods. In fact, it is not uncommon to use added salts merely as diluents for the catalyst, in order to keep the amount of the latter conveniently small. Of the various salts used in this manner, potassium sulfate has been shown to be most effective (*19*) with the possible exception of dipotassium hydrogen phosphate (*8*). The latter compound must be used with great care, and never alone. When mixed with potassium sulfate, up to a little over half of the total, considerably more rapid digestions have been shown to result; greater proportions caused loss of nitrogen. This addition is clearly equivalent to the addition of the phosphate in the form of phosphoric acid, provided the total salt content is maintained with potassium sulfate. Phosphoric acid has been used by many investigators, particularly with the Kjeldahl micromethod, with good results when the proportion of phosphoric to sulfuric acid was carefully controlled. The role of the phosphoric acid is obscure, but its beneficial effect appears to be well established, particularly in the digestion of proteins.

Catalysts. There is most confusion and lack of agreement, and a most voluminous literature, on the role of catalysts. Osborn and Wilkie (*24*), who studied 39 different metals, found mercury superior for protein digestion, followed in order by tellurium, titanium, iron, and copper. Selenium, molybdenum, vanadium, tungsten, and silver were useful under less vigorous conditions.

The superiority of mercury over all other single metallic catalysts seems well established by the work of Osborn and Krasnitz (*23*), Milbauer (*20*), and others. Copper, though widely used because of its convenience, is known to be far less effective, though adequate for many purposes. Selenium, introduced by Lauro, has been the cause of most disagreement between investigators. Certain conclusions drawn from the large amount of work that has been done in studying this catalyst seem to be warranted.

There is little doubt of the effectiveness of selenium as a catalyst, though there is evidence that its chief effect is in shortening the clearing time of the digest. It has been shown repeatedly that the clearing time is no adequate measure of the digestion time, and recent work (*5, 7, 11, 29*) indicates that a digest may clear a long time before the decomposition is complete.

There is little doubt that the quantity of selenium must be kept as small as possible, for an excess tends strongly to lead to the loss of nitrogen.

Selenium apparently causes loss of nitrogen, which increases considerably with the length of digestion time and with the quantity of selenium. The reason for this effect is obscure in spite of studies of the mechanism of selenium catalysis carried out by Sreenivasan and Sadisivan (*30*) and more recently by Patel and Sreenivasan (*25*), who confirm in all respects the above-mentioned effects and recommend against general use of selenium. Maintenance of a high level of sulfuric acid concentration apparently reduces this loss to some degree, as does the use of a combined mercury-selenium catalyst (*25*).

The use of selenium in small quantities in combination with mercury has been approved by a majority of investigators who have tested it (*23, 25, 29, 30*), though the conclusion is far from unanimous. The same can be said for the combination of copper and selenium (*7, 27, 31*). It is doubtful if majority opinion favors a combination of all three catalysts, though many investigators also favor this. Milbauer (*20*), who has investigated this question with considerable thoroughness, recommends the combination of mercuric sulfate and selenium in the ratio of 4 to 1, as the best catalyst. This recommendation should be combined with that of Bradstreet (*3*), who specified an upper limit of 0.25 gram of selenium for a macrodigestion regardless of other conditions of the digestion, and with consideration of the necessity of maintaining an adequate amount of sulfuric acid as compared with both added salt and catalyst.

The question of catalysts, though extensively investigated, has rarely if ever been studied in combination with complete control and study of the other factors of the digestion which may be equally important and are probably interrelated with the catalyst effect.

Oxidizing Agents. Perhaps no other factor in Kjeldahl digestion has been the subject of as much irrational treatment as oxidizing agents. The desire to speed up the digestion by adding an oxidizing agent is understandable, but so is the fact that elementary nitrogen is a more stable form than ammonia nitrogen, and treatment with oxidizing agents may well lead to oxidation of ammonia to nitrogen. Only when there is present a sufficient amount of other reducing agents, which will remove oxidizing agents preferentially as compared with the removal by ammonia or other reduced nitrogen, is the use of an oxidizing agent considered safe. Any violent oxidizing agent such as persulfate, permanganate, or perchlorate is of dubious applicability (*2, 12, 24, 33*). In the early 1900's various highly capable investigators, such as Osborn and Sørensen, employed potassium permanganate successfully. Their success may well be a tribute to their chemical judgment, rather than an endorsement of the procedure. Judicious use of such agents in small quantity, and with digests still rich in carbonaceous reducing agents, is probably a safe procedure. The assumption of such judicious use may well be inapplicable to the routine analyst, who is likely to perform the greater number of Kjeldahl analyses.

Of all the oxidizing agents that have been used or recommended, only hydrogen peroxide seems to have received no criticism whatever. Whether this is due to the inherent merits of this reagent or solely to the inadequacy of investigation is still not clear. As generally used, additions of small amounts of this reagent in the Kjeldahl micromethod do not appear to cause low results (*17, 18, 26*). The reagent frequently contains nitrogen in the form of a preservative, and correction for this must be made by means of a properly determined blank, or high values will result (*15*). Whether this is a factor in the favorable reports on the use of hydrogen peroxide is not clear, though some investigators (*21*) so reporting have been aware of this source of extra nitrogen and corrected their results accordingly. The proper method of addition of the reagent with respect to the stage of the digestion appears to be of importance (*21*). The study on which this was based contained considerable inherent error and variability, but the conclusions are probably valid because they rest on comparative data treated statistically. The influence of hydrogen peroxide on Kjeldahl digestions should be studied further.

Reducing Agents. Oxidized forms of nitrogen require reduction before they may be satisfactorily determined by the Kjeldahl method. There are several satisfactory reducing agents for all but perhaps nitrate nitrogen, and this can with some difficulty be quantitatively reduced also. More difficult is the question of determining certain ring forms of nitrogen, such as pyridine and pyrrol derivatives. These forms of nitrogen appear to respond to reducing agents, but better to combined reducing and hydrolyzing agents such as hydriodic acid. The classical work of Friedrich, Kuhaas, and Schnurch (*9*) on this subject has probably not been bettered. Jonnard claims that some of the nitrogen of proteins, presumably that contained in tryptophan, histidine, or proline, is not completely recovered without the use of some agent such as hydriodic acid. Although this statement has not been refuted, we can at this stage at least hope that this investigator is wrong. Considering the large number of protein analyses that are performed, it would be little less than tragic if each required preliminary reduction and hydrolysis before being subjected to the Kjeldahl digestion.

Time and Conditions of Digestion. There seems to be little general agreement as to the time necessary for digestion, particularly in the analysis of protein nitrogen. Clearly this factor is modified greatly by the conditions of the digestion, such as the catalyst, and addition of oxidizing agents. Most striking are such recent studies as those of Jonnard and of Chibnall, Reese, and Williams, who find that it is necessary to continue digestion for as much as 8 to 16 hours to obtain maximum yield of nitrogen, and, in fact, to employ this long time even with a stringent set of digestion conditions, including the use of selenium, reducing agents, and added salts. On the other end of the scale are the recent studies of Miller and Miller (*21*), who, using nothing but straight sulfuric acid and hydrogen peroxide, no catalyst, salt, or other aids, claim complete recovery of nitrogen from even the most refractory proteins in 9 to 15 minutes. The number of clinical methods in which some 20 minutes' digestion is used is very considerable, and probably includes most of the clinical analyses performed. Whether these methods by virtue of their low accuracy simply fail to show the errors caused by the short digestion is a question. Even allowing for this effect, it remains difficult to explain the enormous discrepancies between the digestion times adopted by various investigators.

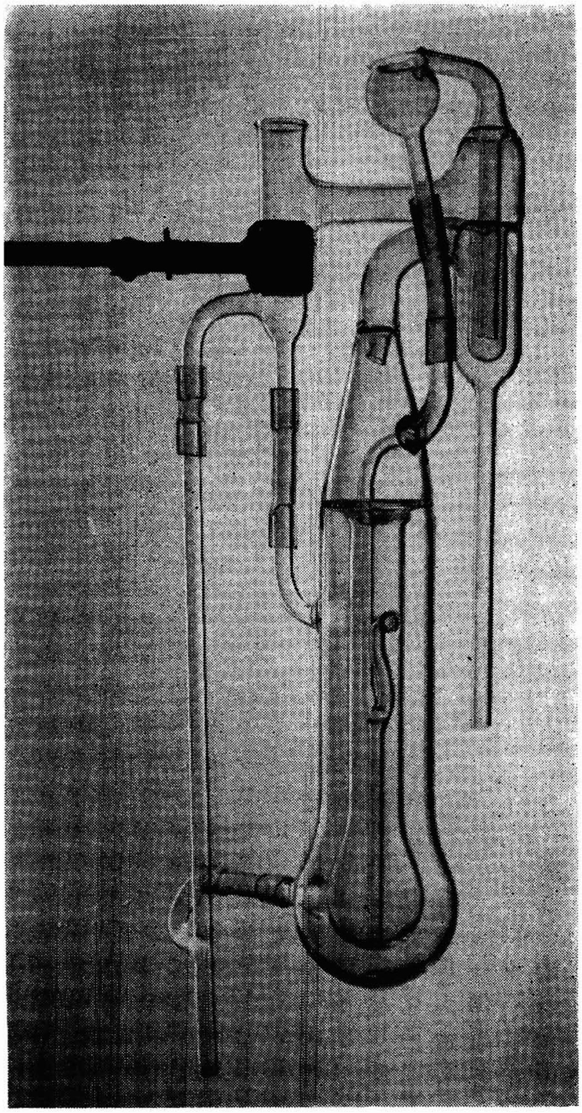

Figure 1. Distillation Apparatus

Standardization of an inadequate method against known amounts of nitrogen has been practiced with some success, but this is not a desirable procedure in working with unknown forms of nitrogen.

KJELDAHL MICROANALYSIS

Because there is no doubt that any competent analyst can distill and determine the ammonia of a Kjeldahl digest, or indeed can determine the ammonia without distillation by colorimetric procedures, or can titrate it by a variety of methods, it seems desirable to discuss only that phase of the determination of the ammonia in which new technique is still being developed rapidly—viz., the Kjeldahl micro and ultramicromethods.

With quantities in the milligram range there are several rapid, accurate, and highly satisfactory steam-distillation procedures. The author naturally prefers the equipment and technique developed by him (*14*), although no claim is made for other than purely technical advantages.

The apparatus shown in Figure 1 is made as a single piece of glass, with a steam generator surrounding the distillation flask, and an internal cold finger condenser, which gives a rugged and compact unit that is nearly automatic in its operation. Figure 2 shows a convenient type of mounting for the distillation apparatus, which carries a movable burner, receiver holder on a rack and pinion, and built-in piping for gas and water. Multiple apparatus may be obtained for any desired number of Kjeldahl distillation units (obtainable from the Microchemical Specialties Co., Berkeley, Calif.).

About 8 minutes are required for the complete distillation with this equipment, a time somewhat in excess of that specified for some other types of apparatus, because of the necessity of heating the small amount of cold water to boiling. The simultaneous use of two sets of apparatus by the analyst not only cancels this increased time but increases considerably the daily output of analyses over most other types of equipment, because most of them do not readily allow for operation of more than one unit at a time. The convenience and the saving in time and reagents of the milligram scale Kjeldahl over all Kjeldahl macroprocedures are so great that it is difficult for one familiar with both to understand why any Kjeldahl macroanalyses should ever be performed. There is no loss in accuracy and the expense of installation is a fraction of that of the large scale equipment.

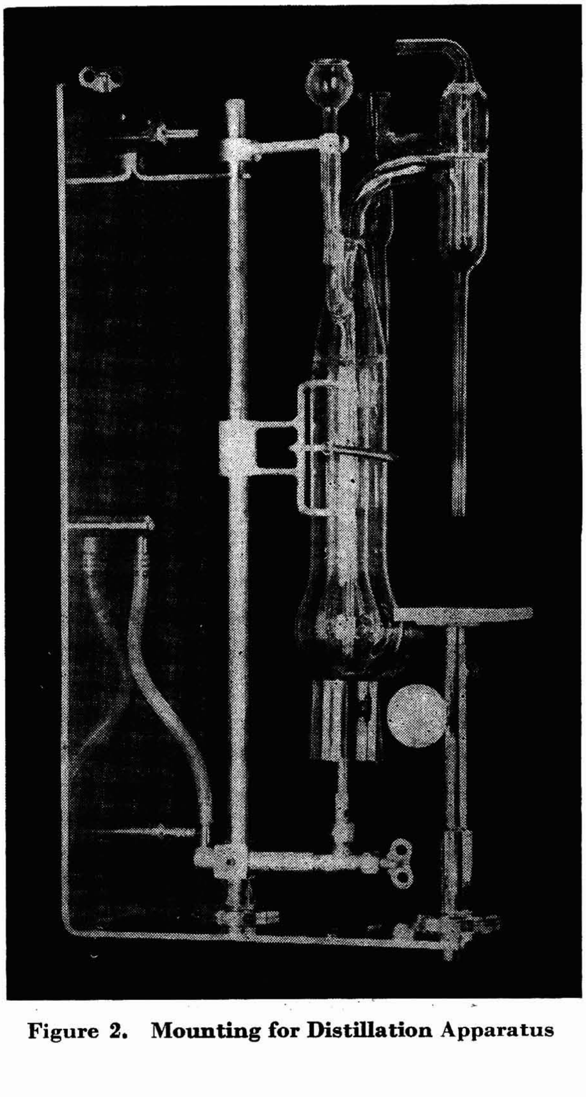

Figure 2. Mounting for Distillation Apparatus

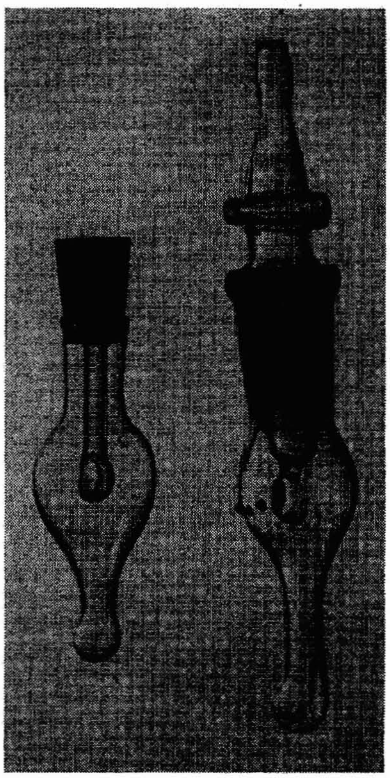

Figure 3. Digestion Bulb

KJELDAHL MICROGRAM ANALYSIS

More interesting perhaps than the milligram range is the ultramicro or microgram range of analysis, in which the nitrogen in the sample may amount only to 1 or a few micrograms. As early as 1934, Kirk (*15*) demonstrated that 1 or 2 micrograms of ammonia nitrogen could be distilled quantitatively by a combination of boiling and aeration. Other investigators have used aeration to separate very minute amounts of ammonia, but it is generally recognized at present that the diffusion technique originated by Conway and Byrne (*6*) is the most satisfactory method of removing ammonia from a micro-Kjeldahl digest (*22*). This procedure is generally used today wherever Kjeldahl nitrogen ultramicroanalysis is performed, particularly in the Carlsberg Laboratory by Brüel, Holter, Linderstrøm-Lang, and Rōzits (*4*), whose procedure will detect amounts as small as 0.005 microgram of ammonia nitrogen and may be used with a total sample as small as 0.1 microgram. Technically the method is complex and exacting. A total time of about 2 days elapses during the digestion alone, a factor which effectively excludes the method from general or routine use, and makes it valuable only for very special research purposes. It has the distinction of representing probably the most delicate titration procedure so far described, as well as the quantitative transfer of the smallest quantities of ammonia by diffusion.

Slightly less sensitive but more practical in general use is the method of Tompkins and Kirk (*31*), which has not been applied to less than 0.5 microgram of total nitrogen and has a sensitivity of about 0.01 microgram, or roughly one half the sensitivity of the Carlsberg Laboratory method discussed above. The total elapsed time of a determination is of the order of 4 hours, and with enough equipment a single analyst can complete up to 30 complete analyses in a single working day.

The apparatus consists of a stoppered bulb-shaped vessel with a tubular extension terminating in a small digestion bulb, as shown in Figure 3, which includes a rubber-stoppered vessel for use at ordinary pressures and a glass-stoppered vessel for use in vacuum diffusion. The sample is digested with 0.1 ml. of 50% by volume sulfuric acid containing a little copper selenite. Mercury catalyst and other combinations of digestion fluid have been used at times. The digest is neutralized by sodium hydroxide layered under the acid digest. The small glass cup attached to the stopper carries the standard acid in which the ammonia is collected. The volume of standard acid is only 50 λ (1 λ = 10^{-6} liter = 0.001 ml.), and it is contained in the small cup whose rim has been lightly greased with vaseline, so that the drop of acid will not spill, regardless of how the cup is turned. After the vessel is sealed, the digest is mixed with the sodium hydroxide and the mixture is used to wash all the walls, thereby neutralizing the acid that has condensed on the walls of the vessel during the digestion.

Three hours' diffusion at room temperature or incubator temperature or 0.5 hour in vacuo serves to transfer the ammonia quantitatively to the standard acid in the receiver. The excess acid is titrated as usual, using a capillary buret which can be read to a sensitivity of 0.02 λ. The method is accurate to about 1% and has an approximate lower limit of 0.5 microgram of total ammonia nitrogen.

In the writer's opinion, this is the most practical of the ultramicro or microgram Kjeldahl methods, inasmuch as it is relatively rapid, requires a minimum of difficult manipulation, and is accurate and simple. Its application to the analysis of proteins and other difficultly digestible forms of nitrogen has not been completely studied, though it has been shown that the microgram method checked accurately with the milligram method on the same protein solutions, and in fact yielded a superior precision as compared with the milligram method.

It does not appear that the lower limits of sensitivity of microgram Kjeldahl analysis have been reached, though it is probable that the accuracy in the present range will not be greatly improved by future developments. To do so would require substantial improvements in the accuracy of the Kjeldahl macromethod, because there are errors of unknown or only partially understood nature in all Kjeldahl digestions which will not be eliminated by working on a smaller scale. It can be safely predicted that the limits of analysis will be lowered by at least a factor of 10 and possibly as much as 100- to 1000-fold. Such developments are now being studied and some progress has been made. The only methods of determining ammonia which offer greatly increased sensitivity are spectrophotometric in nature. For spectrophotometry the Nessler method is not completely suitable because of the colloidal form of the colored compound and other inherent difficulties.

Van Slyke and Hiller (*32*), about 1933, and later Borsook (*1*) applied the sodium phenate and hypochlorite colorimetric method for determining ammonia colorimetrically, a method which apparently has several points of superiority over the Nessler method, including at least as great sensitivity and a truly soluble colored product. Under proper conditions, this color apparently obeys Beer's law. Because the spectrophotometer may be made to yield enormous sensitivity by proper design of the absorption cell and proper modification of technique, factors of as much as 500-fold increased sensitivity over standard operation were achieved by Kirk, Rosenfels, and Hanahan (*16*), who used capillary absorption cells 5 cm. in length and containing as little as 160 λ of liquid.

Further increases in sensitivity are possible by extending the same principles, and spectrophotometers capable of sensitivities a millionfold greater than present standard operation are within the realm of possibility. These developments may well make it possible ultimately to determine as little as 0.001γ microgram of ammonia nitrogen, or even less, with accuracies of better than 5%. If this can be realized in practice, there is no reason why the single living cell and its component parts may not be subject to analysis and treatment as an experimental object much as whole animals are now used. The possibilities inherent in the range of ultramicroanalysis, far from being exhausted, are just now beginning to be realized and their application to the field of experimental biology can be only vaguely surmised. One of the most important methods used will certainly be the Kjeldahl procedure and it is probably one of the first that will be extended into the range of cellular studies because of its tremendous importance in biological investigation.

SUMMARY

The present status of the Kjeldahl method leaves much to be desired in spite of its wide use and tremendous value to industry, nutrition, physiology, biochemistry, and medicine. Fundamental research is still needed to elucidate and improve the digestion process for use with different forms of nitrogen. The question of reducing and oxidizing agents other than sulfuric acid, and the matter of the proper catalyst, particularly require further fundamental investigation.

Most significant is the rapid development and wide adoption of the micro and ultramicro forms of the Kjeldahl analysis. It is here that many of the most striking and significant developments are still to be expected, particularly in lowering the range of application and applying it to the exploration of minute biological systems, perhaps the living cell itself.

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NOTES ON ANALYTICAL PROCEDURES . . .

Dumas Nitrogen Determination Using Nickel Oxide

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THE Dumas nitrogen determination apparatus previously described by the present author (*4*) has now been used in this laboratory and in several industrial and scientific laboratories during a longer period, and experience has indicated improvements in certain constructional details, which lower the risk of breakage and add to the convenience in using the apparatus.

A schematic view of the apparatus is shown in Figure 1.

In order to avoid the risk of breakage, most of the tapered ground joints have been replaced by ball and socket ground joints, or flat ground joints, held together by clamps. The ball and socket ground joints were satisfactory when kept in a fixed position during use, as is the case with the joints on the combustion tube. The joints between the four-way stopcock and the nitrometers are sealed together with Krönigs glass cement. t_1 and t_2 are flexible metal tubes, connected with the stopcocks through flat ground joints of metal and glass. t_3 and t_4 are glass tubes shaped in a U to provide flexibility. s_2, a special four-way stopcock, replaces two three-way stopcocks in the old apparatus.

A laboratory for mineral oil research, which had to determine small quantities of nitrogen in oil products, wanted a tube filling with a greater oxidation capacity. The part of the tube which is situated in the hot furnace, *k*, was therefore made wider. As this seemed to have no bad influence on the microanalyses, every apparatus is now provided with this wider tube, which makes it possible to carry out more analyses with one tube filling and gives more assurance of complete combustion. Samples of 50 mg. of motor oil are burned with good results, using a combustion time of about 20 minutes. Although the suitability of the nickel–nickel oxide tube filling may be doubted because of the experiments of Bell (*2*), this tube filling has always worked well, in good agreement with the experiments performed by Kurtenacker (*5*).

The part of the quartz tube situated within furnace *k* must have a wall thickness of at least 1.5 mm. During use a thin layer of nickel silicate is formed on the inside of the tube, which seems to protect the quartz from further chemical attack. If the quartz walls are too thin this layer will cause cracking of the tube because of the difference in thermal expansion.

The score in the ground joint of the capsule can be dispensed with, as it has no perceptible influence on the blanks and the necessary washing times, and it is unnecessary to have a plug in the capsule during the combustion. Instead of the plug rod *l* is now used, which is taken out of the tube after the capsule is put in place. The capsule and the rod are provided with a better supporting device, the use of which is shown in Figure 1. Outside the apparatus the capsule is handled with the tweezers, *p* and *r*, and the stand, *d*. The stopper, *m*, for closing the combustion tube has been redesigned (Figure 1); it should be lubricated with silicone grease. The nitrometers, n_1 and n_2, are more rigidly constructed than formerly. The capillaries leading down into the

Table I. Analysis of Nitrogen-Containing Compounds

No.	Substance	Weight of Sample	Pressure	Temperature	N_2	N Found	N Calcd.
		Mg.	*Mm. Hg*	° *C.*	*Ml.*	%	%
1	Glucosamine hydrochloride	11.27	756	24	0.643	6.52	6.52
2	Carbobenzoxyglycine benzhydryl ester	10.59	757	26	0.347	3.73	3.73
3	*N*-Acetyl-*p*-aminosalicylic acid	12.85	762	27	0.810	7.19	7.14
4	D(+)3-Methylhendecanamide (*7*)	11.05	762	26	0.675	6.99	7.03
5	24-Methylpentacosanamide (*1*)	8.943	763	25	0.272	3.50	3.54
6	(+)-2 (L),9(D)-Dimethyltetracosanamide (*7*)	13.124	750	25	0.413	3.56	3.54
7	$\Delta^{21:22}$-Tricosynamide (*8*)	11.524	766	24	0.497	3.99	4.01
8	Diphenyl-*p*-toluidinophosphonate	9.50	748	25	0.352	4.18	4.13
9	Dibenzyl-*p*-toluidinophosphonate	17.22	747	26	0.581	3.79	3.82
10	Dibenzylphenylethylaminophosphonate	9.61	756	24	0.305	3.63	3.67
11	Diphenylaminophosphonate	10.98	756	25	0.543	5.64	5.62
12	*m*-Chloronitrobenzene	7.43	772	25	0.567	8.88	8.89
13	D-2-Methylhexacosanamide (*8*)	11.53	744	26	0.351	3.41	3.42
14	Taurine	10.68	759	26	1.049	11.20	11.20
15	Taurine	3.434	751	21	0.336	11.23	11.20
16	Thiourea	1.525	751	22	0.490	36.74	36.81
17	Urea	1.335	751	23	0.546	46.61	46.65
18	Cyanacetamide	1.036	751	24	0.305	33.44	33.33
19	Silver nitrate	15.16	763	25	1.086	8.24	8.25
20	Motor oil A	42.7	...	..	0.0024	0.007	...
21	Motor oil A	45.9	...	..	0.0025	0.006	...
22	Motor oil B	40.5	...	..	0.0100	0.029	...
23	Motor oil B	43.5	...	..	0.0110	0.029	...
24	Motor oil C	40.2	...	..	0.0025	0.007	...
25	Motor oil C	44.5	...	..	0.0030	0.008	...

Analyses 20 to 25 were carried out in an industrial laboratory, using a special grade of copper oxide and a special type of nitrometer, the construction of which will be subject of a later publication.

mercury are ground oblique at the end to give small bubbles. The funnels of the nitrometers can be closed with rubber stoppers when the apparatus is standing idle.

When the tube is being filled the hopcalite must not be situated too near *k*, which might cause undue heating. The overheated hopcalite will give off gas for a long time, and it will be impossible to get microbubbles. The nickel oxide used in the combustion furnace should be free from metals which reduce carbon dioxide. A specimen of nickel oxide (Baker's analyzed), which according to the manufacturers contained 0.35% of cobalt and 0.02% of iron, was found unsatisfactory for the present method.

If mainly samples containing nitrogen not combined with oxygen are analyzed, the use of metallic nickel in the tube is superfluous. When the tube filling is exhausted it may be reoxidized by leading a stream of oxygen through the hot apparatus for 1 or 2 hours. After a few analyses have been performed, so much nickel has been reduced that even nitro compounds can be analyzed with good results. The author has used his apparatus in this manner without refilling during a whole year. The filling is still in use.

When the capsule has been put into the apparatus for combus-

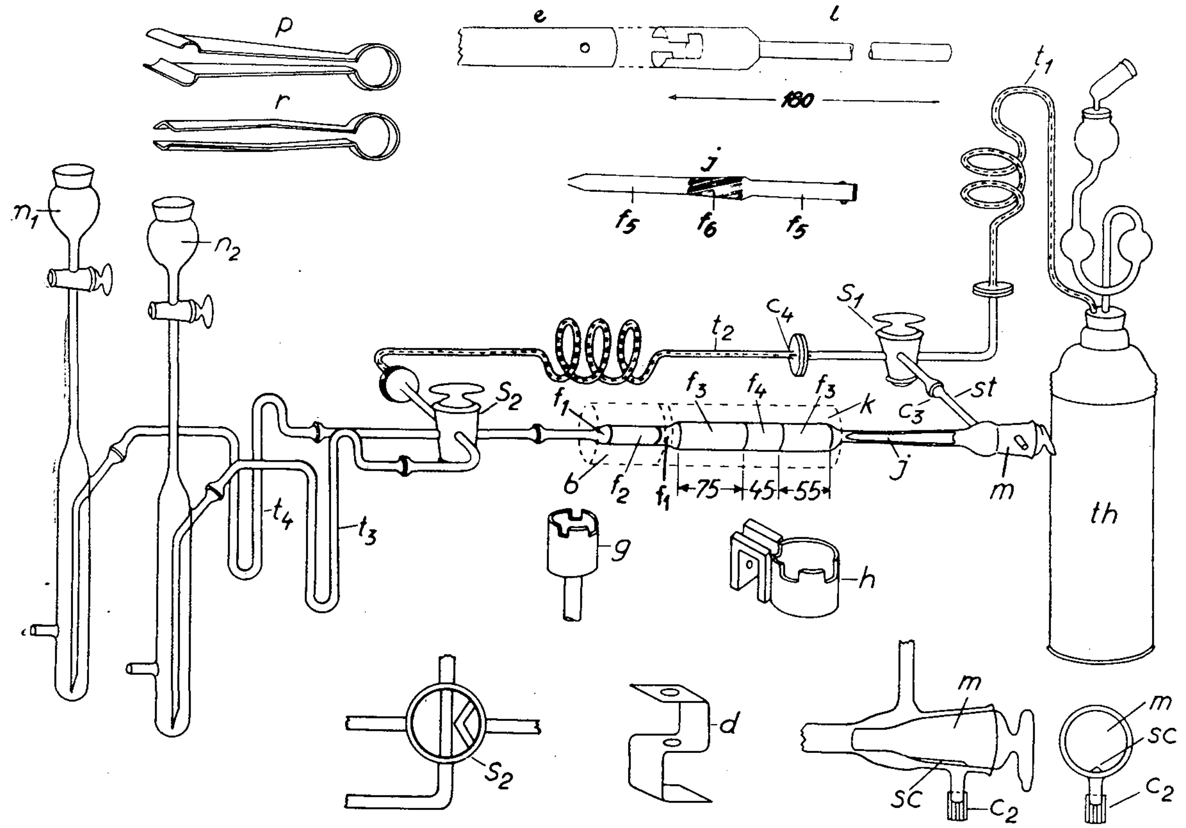

Figure 1. Schematic Diagram of Apparatus

b. Furnace at 100° C.
C_2, C_3, C_4. Capillaries
e. End of capsule
f_1. Quartz wool
f_2. Hopcalite
f_3. Nickel oxide
f_4. Nickel
f_5. Coarse copper oxide
f_6. Sample mixed with fine and coarse copper oxide
g,h. Holders for stopcocks
j. Capsule
s_1. Three-way stopcock
sc. Score in stopper *m*
st. Side tube of combustion tube
th. Thermos flask

tion according to the procedure described (*4*), the backstream is admitted in such a manner that the carbon dioxide passes through both c_4 and *st*. On a few occasions the fine copper oxide clogged the capsule, almost preventing the carbon dioxide from passing through. Atmospheric nitrogen may then remain in the capsule and cause high results. In order to avoid this the procedure has been changed.

When the backstream is turned on, stopcock s_1 is turned in such a manner that the stream passes only through c_4, and no gas passes through *st*. By putting the tongue near c_2, or by putting a rubber tube on c_2 and allowing the gas to bubble through water, it is easy to ascertain that a good stream is passing through the capsule. If this is the case, s_1 is turned so that the stream also passes through *st*. If too little carbon dioxide passes through the capsule, the apparatus is allowed to stand in this position until it can be expected that the atmospheric nitrogen has been swept out of the capsule. The analysis is then continued as described (*4*), although it may be necessary to extend the sweeping time after the combustion.

In the previous paper (*4*) it is stated that the method is not so good that the results differ by less than 0.1% from theory. The author had calculated the difference according to the formula

$$\%\ \text{error} = \left|\frac{\%\ \text{theory} - \%\ \text{found}}{\%\ \text{theory}} \times 100\right|$$

under the mistaken impression that the accuracy claimed by Roth (*6*) was calculated in the same manner. However, Roth used the more general practice of calculating the error according to the formula

$$\%\ \text{error} = |\%\ \text{theory} - \%\ \text{found}|$$

When calculated in this manner the results given in (*4*) differ by less than 0.1% from theory and only one (No. 18) of the results given in the present paper differs by 0.11% from theory.

In the same paper Unterzaucher's work in 1940 (*9*) is referred to as the origin of the backway streaming system used in the present apparatus. The author did not know then that Gysel (*3*) had shortly before (in 1938) used an apparatus with backway streaming for the determination of nitrogen according to Dumas.

ACKNOWLEDGMENT

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+ Separation of Cotton and Rayon or Cotton and Acetate for Analytical Purposes

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THE method given in this paper effects a clean separation of cotton and rayon (regenerated cellulose) or cotton and acetate at room temperature, using a solution of sodium zincate and ammonium thiocyanate. The solutions are readily filterable and no cutting up of the sample is required. The method offers considerable advantages over the one in general use at present (A.S.T.M. D 629–46T, using calcium thiocyanate); the gelatinous condition of rayon solution in calcium thiocyanate causes great difficulties in the separation of the two fibers and gives uncertain results.

Pure undegraded cotton may be completely insoluble in the sodium zincate–ammonium thiocyanate solvent, but because cotton textiles have various histories of kiering, bleaching, long storage, exposure to light, etc., amount of degradation can be expected to be reflected in solubility. The variation, however, is ordinarily small—on the order of 0.5 to 1% in the limited number of samples tested.

A correction of 0.7% is made—added when the result is in terms of per cent cotton and subtracted when in terms of per cent rayon—for kiered cotton fabric, and a correction of 0.5% is made for the same fabric when kiered and partly mercerized. This is the amount lost during treatment with the solvent. The 0.7% correction was also found to apply to one case of cotton fabric after a U.F. resin finish had been removed by 0.5 *N* hydrochloric acid at 60° C. in 1 hour.

PROCEDURE

Make a stock solution from 20 parts by weight of sodium hydroxide, 9 of zinc oxide, and 51 of water by adding an amount of water equal to the sodium hydroxide, stirring (applying further heat if necessary) until all the zinc oxide is dissolved, then cooling and adding balance of water. This solution (double strength) is stable and zincate crystals do not separate from it. The final percentage composition of the solvent is:

Sodium hydroxide	10
Zinc oxide	4.5
Ammonium thiocyanate	10

For samples up to about 4 grams (deresined, desized, etc., and dried) use 100 grams of solvent made by mixing 40 grams of the double-strength stock with 50 ml. of cold water, and press the sample in the solution for a few minutes by means of a rubber stopper attached to a rod. This will swell and disperse most of the rayon. Add 10 grams of ammonium thiocyanate and continue pressing with the rubber stopper for about a minute.

Pour the liquid through an unpadded Gooch filter, using none or very little suction. By pressing with the rubber stopper, remove as much liquid as possible. (A bag made of fine-mesh nylon may be used instead of the Gooch.)

Again add 40 grams of stock and 50 ml. of cold water, work the sample, add 10 grams of ammonium thiocyanate, and press thoroughly for a few minutes. Remove the liquid by the Gooch as before.

Add 40 ml. of water and 10 ml. of strong ammonia and work the sample with the rubber. Remove liquid by Gooch. Repeat with hot water (70° to 90° C.), then with hot 5% acetic acid, and finally with hot water. This removes the zinc, considerable amounts of which otherwise remain.

A final treatment with alcohol may be given to shorten the drying time. The zinc content of the insoluble material (cotton) is negligible—0.1% total ash.

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Direct Titration of Ferric Iron by Stannous Chloride

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As a standard stannous chloride solution may be stored without difficulty, the reaction

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

may be used as the basis of a method for the determination of ferric iron. It is not only possible to carry out the reduction needed for the Zimmermann-Reinhardt method, but Fresenius (*1*) founded upon this reaction a titrimetric determination, later improved by other authors (*2–4, 6*). However, the literature does not show that procedures to facilitate observing the end point of the titration have been used in practice.

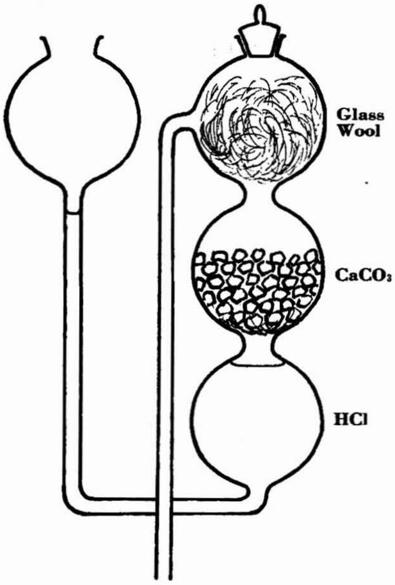

Figure 1. Apparatus

Height of apparatus, 150 mm.
Diameter, 40 mm.

Experiments performed by the authors indicate that the above reaction enables the elaboration of an accurate and rapid analytical method. Because the reaction progresses a little slowly, especially toward its end, the sample should be heated to 60° to 70° C. and the acid concentration kept about pH 0.6. Added ammonium chloride also accelerates the process. To exclude oxygen, an atmosphere of carbon dioxide in the titration flask is indispensable.

A double indicator is used to show the end point. The reduction of most of the ferric ion is indicated by thiocyanate, and then if the solution is straw-yellow ammonium molybdate is added. In the presence of phosphate the molybdate is reduced by stannous chloride to molybdenum blue. The same reaction takes place in the presence of silica, arsenate, or germanate, but these cannot be used as indicators. On addition of molybdate the solution becomes green, changing to blue at the end point. The reduction of molybdate requires phosphate ion in order to increase the oxidation potential of molybdate. Thus the phosphomolybdate indicator can be used only at low ferric concentration; otherwise the ferric ions bind the phosphoric acid as a complex and the molybdenum blue reaction cannot take place. The reaction described is reversible.

REAGENTS

Stannous Chloride, 0.1 *N*. In order to avoid the oxidation of stannous chloride, in preparing the solution 80 ml. of concentrated hydrochloric acid are poured into the storage bottle for each liter of final solution, and several pieces of marble are dissolved in it to expel the oxygen. Then 12 grams of crystalline stannous chloride are added per liter, and after it has dissolved the solution is made up to the required volume. The solution is stored in a bottle directly connected with the buret (*5*). A carbon dioxide atmosphere is maintained over the solution by an automatic apparatus that fits into the stopper of the flask (Figure 1).

The solution may be standardized against 0.1 *N* potassium bromate solution. Into a titration flask with a narrow neck are introduced 1 ml. of concentrated hydrochloric acid, several marble fragments, one or two crystals of potassium bromide, and 4 drops of a rubrophen solution or of methyl orange indicator. Then 20 ml. of stannous chloride are added and the sample is titrated rapidly until it becomes completely colorless. The titer does not change appreciably on storage: July 1, 0.8970 *F;* October 2, 0.8850 *F*.

Potassium thiocyanate solution, 4.85 grams per 100 grams of water.

Ammonium molybdate solution, 1.96 grams per 100 grams of water.

Sodium phosphate solution, 1.1 grams per 100 grams of water.

Ammonium phosphomolybdate solution, 1.9 grams per 100 grams of dilute ammonia.

Table I. Titration of Ferric Iron

(Indicator: 4 drops of ammonium molybdate and 3 drops of sodium phosphate)

Fe Taken *Mg.*	Fe Found *Mg.*	Difference *Mg.*	%
10.96	11.11	+0.15	+1.35
16.45	16.31	−0.14	−0.85
21.93	21.88	−0.05	−0.22
32.90	32.87	−0.03	−0.09
43.87	43.84	−0.03	−0.06
54.84	54.74	−0.10	−0.18
82.26	82.16	−0.10	−0.12

Table II. Titration of Ferric Iron

(Indicator: ammonium phosphomolybdate, 3 drops)

Fe Taken *Mg.*	Fe Found *Mg.*	Difference *Mg.*	%
2.57	2.51	−0.06	−2.33
5.15	5.23	+0.08	+1.55
20.60	20.52	−0.03	−0.38
30.90	30.99	+0.09	+0.29
41.20	41.19	−0.01	−0.02
82.40	82.04	−0.36	−0.43
92.70	92.56	−0.14	−0.15
103.00	102.75	−0.25	−0.24
154.50	153.50	−1.00	−0.66

PROCEDURE

Twenty milliliters of the solution to be tested, containing 3 to 150 mg. of iron, are pipetted into a 100-ml. flask with a narrow neck and acidified with 1 to 2 ml. of concentrated hydrochloric acid. Then 1 gram of ammonium chloride is added, the mixture is heated to about 60° to 70° C., and 2 to 3 drops of thiocyanate solution and several pieces of marble are added. The lively ef-

Table III. Batch Analyses

(57.64 mg. of iron taken)

Fe Found *Mg.*	Added Foreign Ion	*Mg.*	Difference *Mg.*
57.90	Cu	5	+0.26
57.93		25	−0.29
57.90		50	+0.26
57.64	W	13	0.0
57.67		31	+0.03
57.69		52	+0.05
57.61	As^{III}	4	−0.03
57.66		16	+0.02
57.69		80	+0.05
57.59	As^{V}	1	−0.05
57.69		2	+0.05
57.61		10	−0.03
57.74	Sb^{V}	7	+0.10
57.67		70	+0.03

fervescing solution is titrated by stannous chloride until its color pales to straw-yellow. Then 4 drops of molybdate and 3 drops of phosphate solution are added and the titration is continued until the color changes from green to blue. The last few drops are added slowly, to allow time for the reaction to take place. The procedure, however, does not last more than 1.5 minutes.

The accuracy of the method is illustrated by the data of Tables I and II.

Because aluminum, manganese, zinc, lead, tungsten, and arsenic do not interfere, the procedure is especially efficient for the determination of iron in ores. A small amount of copper does not interfere, but if there is much more copper than iron, the end point is uncertain. Antimony if oxidized to the pentavalent state causes no interference. The procedure cannot be used in the presence of vanadium. Table III gives data obtained in batch analyses.

The suggested method has the advantage that the standard solution can be readily prepared and stored and no special equipment is required for observation of the end point.

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Assembly for Positioning Cuvettes Used for Microanalysis with Beckman Spectrophotometer

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THE new cuvette holder discussed, with carriage and mechanism for positioning it, is especially suitable for the micro adaptation of the Beckman spectrophotometer as described by Lowry and Bessey (*1*). These workers adapted the Beckman spectrophotometer for the colorimetric estimation of extremely small quantities of material. They substituted cuvettes (Pyrocell Manufacturing Company, 207 East 84th St., New York, N. Y.) whose widths are two tenths that of ordinary cuvettes without decreasing the length of the light path (1 cm.), and reduced the depth of the solution necessary for analysis to several millimeters by placing a diaphragm having a hole 1.5 mm. in diameter in front of the exit slit of the instrument.

These modifications make it possible to carry out an analysis on 50 cu. mm. of fluid with approximately the same accuracy as the macromethod. It is essential, however, when using the micro adaptation that the cuvettes be reproducibly positioned within a limit of 0.25 mm. on either side of their centers, because the pencil of light emerging from the hole in the diaphragm is but 0.5 mm. less than the width of the cuvettes. The operator is handicapped in carrying out this exact positioning by two structural elements of the spectrophotometer. First, the construction of the carriage which carries the cuvettes is of light weight and is supported only centrally, so that considerable care must be exercised to prevent minor fluctuations in the position of the cuvettes. Secondly, the cuvettes cannot be positioned easily in the individual compartments of the cuvette holder. This makes it difficult to bring the separate cuvettes into juxtaposition with the light beam when the carriage is moved from one detent to another. In practice, the positioning has to be made frequently by fixing the cuvettes tightly against the spring of the individual cuvette compartments by means of wooden shims.

In the author's experience it has been necessary to place shims on both sides of some of the cuvettes to accomplish the necessary positioning. In other words, this positioning has to be done in part by moving the cuvettes independently from the cuvette holder. Although good analytical results can be obtained despite this difficulty, so much experience and patience are required that in many laboratories it is customary to leave the cuvettes fixed in position throughout a long series of analyses. This is sometimes a disadvantage, as it becomes difficult to clean the cuvette surface in case of spillage or other accident.

To correct these shortcomings a new type of holder for the cuvettes, a new carriage, and a new mechanism for moving the carriage have been constructed (Figure 1).

The cuvette holder is constructed by milling a trough from a solid piece of brass, the width of the trough being about 1 mm. more than that of the cuvettes, and the depth being such that when the cuvettes are in place the light beam will just clear the lower surface. This makes it possible to use a minimum quantity of fluid for analysis. The extra millimeter of space is provided to hold a phosphor bronze spring, which is split into four leaves, so that the cuvettes are separately held tightly against the front of the cuvette holder. The spring extends about halfway down the surface of the cuvette. A second spring is placed near the end of the cuvette holder to press the four cuvettes tightly against each other. Holes are drilled at suitable levels in the face of the cell holder to permit passage of the light. A handle is attached to the holder to facilitate placing it in the carriage.

The carriage consists of a brass base, on either end of which upright strips of spring phosphor bronze are soldered. The cuvette holder fits snugly between the upright strips and rests solidly on the base. The outside dimensions of the holder are

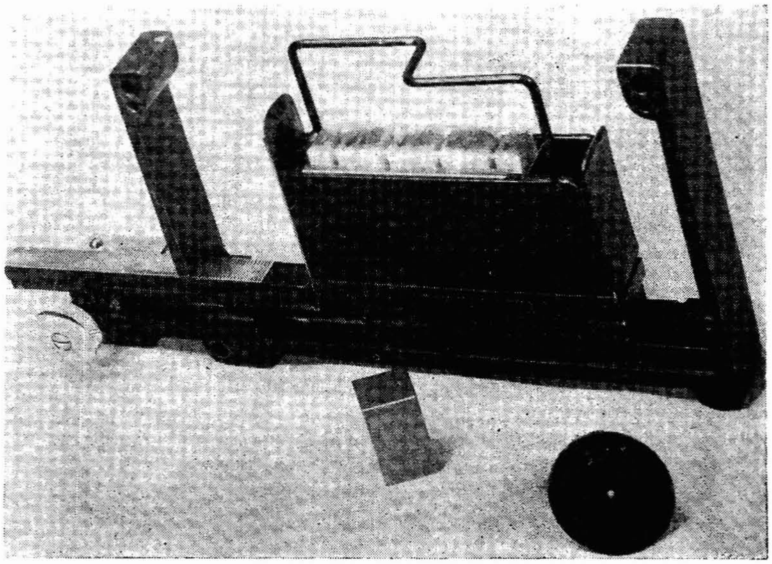

Figure 1. Cuvette Holder, Carriage, and Mechanism for Moving Carriage

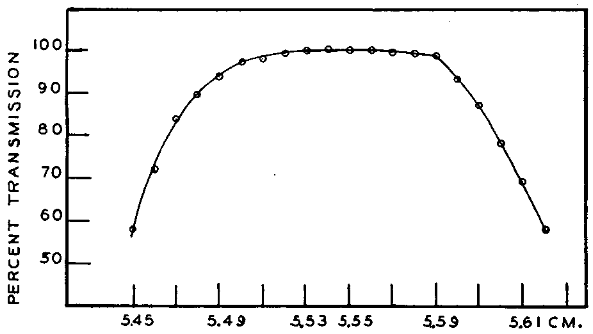

Figure 2. Positioning of Cuvette

exactly the same as those for the ordinary one supplied with the Beckman spectrophotometer for holding macrocuvettes. This permits ready interchange of cuvettes, depending on whether micro or macroanalysis is to be performed.

The mechanism for moving the carriage is made from parts of a mechanical stage for a microscope. A long piece of brass 0.25 inch (0.6 cm.) thick is attached to the slide mechanism, and a slot is sawed into the wall of the casing of the Beckman spectrophotometer compartment to connect with the exterior. Onto the outside end of the strip of brass is fastened a centimeter rule; alongside this rule and fixed in position a vernier is placed. The mechanism is easily adjustable to 0.1 mm. In the assembly pictured (Figure 1) the screw for positioning the carriage interferes with the adjustment knob on the photocell compartment of the spectrophotometer which is used to change from one photocell to another. Rather than make the base for the carriage inconveniently long, this knob was eliminated.

In addition to these changes, a diaphragm of a size that will just fit into a well made around the hole serving as the exit for the light from the spectrophotometer is substituted for the penny diaphragm. The fit is made so exact that the diaphragm requires no accessory fastening mechanism; it can be readily removed by suction or use of a pin inserted into the hole. A diaphragm whose hole is 1.4 mm. in diameter is shown in Figure 1. The data reported below were obtained using a diaphragm having 1.6-mm. hole. Incidentally, the diaphragm cuts down the light sensitivity of the instrument by decreasing the effective area of the light beam. With the 1.6-mm. diaphragm this amounts to 9%. Accordingly the diaphragm cannot be used with the very short wave lengths.

Table I. Reproducibility of Readings Made on Four Cuvettes Following Removal and Reinsertion into Cuvette Holder

Cuvette No.	Per Cent Transmittance Readings with Water, λ = 500 mμ					
1	100.0	100.0	100.0	99.6	100.0	100.3
2	99.7	99.0	99.9	99.1	99.9	99.7
3	100.1	99.3	100.0	99.1	99.6	99.7
4	99.1	99.0	99.9	99.8	99.9	100.5

Figure 1 also shows a dummy cuvette made from brass, which can be used as a substitute for a glass cuvette in case of breakage.

The position at which readings should be taken for the four cuvettes is readily determined by direct experiment. Water or some suitable solvent is placed in the cuvettes in quantities of 50 cu. mm. or more, and the cuvettes are positioned until a maximum reading is obtained. Figure 2 shows a plot of the per cent transmittance (where the maximum is set arbitrarily at 100%) as a function of the position of a cuvette. A maximum reading is obtained over a range of approximately 0.4 mm., the amount of light decreasing on either side of this setting because of occlusion by the cuvette wall. The cuvette should be positioned in the middle of this range when an analysis is performed, to minimize any inexactness in positioning the cuvette. In this instance the proper position of cuvette 1 is 5.55 cm. The position at which readings should be taken for the other three cuvettes is determined in like manner. For the present apparatus these are 1.62, 2.92, and 4.23 cm. One advantage of the apparatus described is that the proper position for the cuvette can be readily checked at any time by simply moving the carriage forward or backward to determine whether there is any further increase in the amount of light. The time required for positioning the cuvettes is not significantly greater than that required with the usual slide mechanism.

Illustrative results obtained using the described modification are presented in Tables I and II. Table I shows the variations encountered in readings as a result of repeatedly removing the cuvettes from the cuvette holder between series of readings. Fifty cubic millimeters of water were used as a sample. The maximum variation in 24 readings was about 1.5% and the average difference in any one set of readings was 1.0%. As the reading for the first cuvette in any one set of values shown in the table was not brought back arbitrarily to 100%, the observed variations include change in output from the lamp.

Table II. Reproducibility of Replicate Determinations of Absorption of Vitamin A in Kerosene-Xylene

Cuvette No.	Per Cent Transmittance, λ = 328 mμ						
	Blanks	Vitamin A					Average
1	100.0	100.0	100.0	100.0	100.0	100.0	...
2	100.0	73.7	72.3	73.1	73.0	73.5	73.13
3	99.8	73.5	72.3	73.1	73.0	73.7	73.13
4	100.3	73.9	73.0	73.6	73.2	72.6	73.26

Table II shows the variation in readings encountered in making repeated measurements of the absorption of vitamin A in kerosene-xylene. Column 2 shows that the blank values between different cuvettes varied less than ±0.3%. Columns 3 through 7 show that the greatest variation between samples was 1.6%, and that the variation between average values for the three cuvettes was less than 0.15%. All measurements were performed on 50 cu. mm. of solution. The cuvettes were cleaned with acetone between measurements but were not removed from the cuvette holder.

SUMMARY

An assembly for holding and positioning the cuvettes used with the micro adaptation of the Beckman spectrophotometer is described. The system offers the following advantages: The cuvettes can readily be removed and replaced in the cuvette holder without introducing significant change in the amount of light transmitted; they can be quickly and reproducibly brought into exact alignment for taking readings.

ACKNOWLEDGMENT

The assembly described was constructed by John Linden, J. H. Emerson Company, Cambridge, Mass., who was also responsible for much of its design. The author wishes to thank June Twomey for technical assistance.

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RECEIVED January 31, 1949.

Correction

In the article on "Determination of Unsaturation in Dehydrogenated Dichloroethylbenzene" [Marquardt, R. P., and Luce, E. N., ANAL. CHEM., **21**, 1194 (1949)], on page 1195, second column, under the heading "Reagents," and on page 1196, first column, line 4 1.0 *N* sodium hydroxide should have been specified, not 0.1 *N* as stated.

Lithium Aluminum Hydride as a Reagent for the Determination of Water

BERTSIL B. BAKER, JR., AND WILLIAM MARSHALL MACNEVIN
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FINHOLT, Bond, and Schlesinger (*2*) state that lithium aluminum hydride reacts vigorously with water according to the following equation:

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 4H_2 \qquad (1)$$

The reagent was subsequently reported suitable for the determination of active hydrogen in organic compounds (*6, 11*), and Reaction 1 was used to determine the strength of lithium aluminum hydride–ether solutions (*5*). No study has been reported, however, of the possibility of using the reagent to determine water. Such a method appeared to offer the advantages of rapid reaction and high sensitivity, inasmuch as a 10-gram sample containing 0.1% water would, by Reaction 1, give over 10 ml. of hydrogen.

The prospect of rapid reaction is of special interest, for almost all other hydrogen evolution methods require from 1 to 48 hours' reaction time, usually owing to the insolubility of the reagent in the sample. This difficulty is not encountered here because lithium aluminum hydride is soluble in diethyl ether (*2*) and certain other organic solvents (*2, 9, 11*). The reagent would thus appear to be especially suitable for the determination of traces of water in organic liquids with which it is unreactive. Alcohols (*9*), acids (*9*), and amines (*8*) react to release hydrogen and must be absent. Aldehydes, ketones, esters, acid chlorides, acid anhydrides, and nitro compounds react (*7*) with lithium aluminum hydride, but do not evolve hydrogen. If an excess of reagent were employed, small amounts of such compounds might be permitted. Completely unreactive toward the reagent are ethers and aliphatic and aromatic hydrocarbons.

An investigation was therefore undertaken to determine the suitability of lithium aluminum hydride as a reagent for water. The experiments did not lead to a precise analytical procedure, but the reagent does seem to be suitable for an approximate analysis (about ±0.005% in a concentration of 0.1%). Perhaps more important, however, the experiments furnished data to show that the reaction in the presence of excess lithium aluminum hydride does not stop with Reaction 1, but proceeds further, probably by one of the paths discussed below.

EXPERIMENTAL PROCEDURE AND RESULTS

Measurements were made of the pressure of the hydrogen evolved in a closed brass vessel upon reaction of known amounts of water with excess reagent. From 10 to 40 ml. of approximately 1% solution of lithium aluminum hydride in diethylene glycol diethyl ether were added to the vessel and from 15 to 50 mg. of water were introduced by means of a hypodermic syringe through a serum bottle–type stopper. The weight of water was determined by difference from the weights of the syringe. The mole ratio of hydrogen to water was calculated. Values ranged between 1.40 and 1.60, depending upon the exact conditions of the experiment. For analytical purposes it was found possible to establish an empirical mole ratio, which, with careful duplication of temperature, degree of agitation, and reaction time, could be reproduced to ±5%. The reaction occurs very rapidly at first and runs sufficiently far in about 1 minute to give mole ratio values of around 1.40. It then slows down considerably, but continues perceptibly for about 1 hour. At the end of this time pressure readings are constant and give mole ratio values approaching 1.55 to 1.60.

STOICHIOMETRY OF REACTION

Both Schlesinger (*2*) and Krynitsky (*5*) gave Equation 1 for the reaction of lithium aluminum hydride with water. However, Krynitsky's hydrolysis was carried out, not with water, but with an excess of 10% sulfuric acid. The acid neutralized the aluminum hydroxide formed and probably prevented any of the further reactions proposed below. Schlesinger added an excess (exact amount not specified) of water dropwise to a dilute (concentration not given, but solubility is only 0.1 gram in 100 grams of dioxane) solution of a weighed amount of lithium aluminum hydride in dioxane and then measured the amount of hydrogen evolved and analyzed the solution for lithium and aluminum to establish the formula $LiAlH_4$. The most likely explanation for the disagreement between the 1.00 ratio of Schlesinger's equation and the 1.4 to 1.6 of this investigation is that when lithium aluminum hydride instead of water is in excess, the reaction does not stop with Reaction 1 but proceeds further by either of the two courses given below.

Dehydration of $Al(OH)_3$:

$$4LiAlH_4 + 16H_2O \longrightarrow 4LiOH + 4Al(OH)_3 + 16H_2 \qquad (1)$$

$$4Al(OH)_3 + 2LiAlH_4 \longrightarrow 2LiOH + 3Al_2O_3 + H_2O + 8H_2 \qquad (2)$$

$$6LiAlH_4 + 15H_2O \longrightarrow 6LiOH + 3Al_2O_3 + 24H_2 \qquad (3)$$

$$\text{Mole ratio } H_2/H_2O = 1.60$$

Amphoteric Reaction of $Al(OH)_3$:

$$2LiAlH_4 + 8H_2O \longrightarrow 2LiOH + 2Al(OH)_3 + 8H_2 \qquad (1)$$

$$LiOH + 2Al(OH)_3 \longrightarrow LiH(AlO_2)_2 + 3H_2O \qquad (4)$$

$$2LiAlH_4 + 5H_2O \longrightarrow LiOH + LiH(AlO_2)_2 + 8H_2 \qquad (5)$$

$$\text{Mole ratio } H_2/H_2O = 1.60$$

Because the ratio of lithium aluminum hydride to hydrogen in both Reactions 3 and 5 is the same as in Reaction 1, their postulation is not in conflict with Schlesinger's data. Schlesinger did not report any investigation of the hydrogen-water ratio.

In regard to the first of the two possible courses (dehydration), if one considers aluminum hydroxide as $Al_2O_3.3H_2O$, an explanation for the above-mentioned decrease in reaction rate when the ratio 1.40 is reached may lie in stepwise reaction of the three water molecules, the third being more difficult to remove and reacting more slowly.

As for the second possibility (amphoteric reaction), a recent article by Gibb (*3*), which appeared after the majority of this work had been completed, stated that the reaction with water is approximately represented by the equations:

$$LiAlH_4 + 2H_2O \longrightarrow LiAlO_2 + 4H_2$$

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 4H_2$$

No discussion or data were given.

Although the amphoteric reaction of aluminum hydroxide with lithium hydroxide has not been studied under conditions similar to those existing in this experiment, it would appear from the work of Allen and Rogers (*1*), Prociv (*10*), and especially Horan and Damiano (*4*), that the acid aluminate, $LiH(AlO_2)_2$ (Reaction 5), is normally formed instead of $LiAlO_2$ as suggested by Gibb.

SUMMARY

The reaction of excess lithium aluminum hydride with water differs from that reported by Schlesinger (*2*) as taking place when water is in excess. The stoichiometry of the reaction is discussed and possible equations are proposed.

A mole ratio of H_2/H_2O of 1.50 to 1.60 was found after the reaction had been allowed to go to completion. This is in fair

agreement with the calculated ratio from either of two proposed reactions.

The establishment of an empirical ratio of hydrogen-water shows the reagent can be used for an approximate determination of water. The reagent may find application in the determination of traces of water in hydrocarbons.

ACKNOWLEDGMENT

The authors are indebted to Hanns K. Anders and George A. Simmons, Jr., for helpful suggestions and aid in obtaining experimental data.

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RECEIVED March 11, 1949. The work described in this paper was carried out, in part, under contract between the Air Matériel Command, Wright-Patterson Air Force Base, and The Ohio State University Research Foundation.

Quantitative Determination of Monomethylol and Dimethylol Urea

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A METHOD for the determination of mono- and dimethylol urea, given by Walter (*10*), was patterned after Folin's method for the determination of urea (*5*) and consists of heating the urea derivative in a solution of magnesium chloride hexahydrate in the presence of concentrated hydrochloric acid. In the process the methylol groups are split off as formaldehyde, the carbonyl groups go to carbon dioxide, and the nitrogen goes to ammonia. The method has the objection that special means are necessary for absorption of the hydrochloric acid fumes. Crowe and Lynch (*1*) have recently given an account of a method for the analysis in acid solution; however, they give no upper limit of concentrations used and the method takes at least 48 hours to complete, inasmuch as dissociation has a half-life of about 10 hours at room temperature.

The method presented here is carried out in dilute solutions and dispenses with the use of hydrochloric acid in the decomposition. In it the methylol ureas are hydrolyzed to urea and formaldehyde; the resulting solution is then analyzed for formaldehyde. It was found that sodium phosphate at a concentration of approximately 0.3 *N* in the neutral pH range will accelerate the dissociation of mono- or dimethylol urea nearly 100 times, and if the solutions are sufficiently dilute so that the equilibrium and the polymerization effects are negligible the dissociation is 99% complete. The advantages of a neutral solution are obvious, for in acid solution the methylol ureas are transformed to a white insoluble solid.

Table I. Analysis of Dimethylol Urea

Time of Heating, Min.	Iodine, Ml.	H_2CO, %
15	54.3	46.5
30	55.6	48.0
60	57.2	49.3
Theoretical	58.1	50.0

Method of Synthesis. Monomethylol and dimethylol urea have been synthesized by the method of Einhorn and Hamburger (*3*, *4*). However, the preferred method is a variation of one given by Walker (*8*) which was taken from Ripper (*6*), Schmibing (*7*), and Walter (*9*), and is carried out in substantially neutral solution. The melting points for the thoroughly dried material were 125° C. for dimethylol and 111° C. for monomethylol urea.

Analytical Procedure. The sample (0.0655 gram) of dimethylol urea was dissolved in 100 ml. of water, 40 ml. of 1 *M* sodium dihydrogen phosphate were added to 20 ml. of 1 *M* sodium hydroxide, and 40 ml. of water were added to make 100 ml. The two solutions were mixed in a 250-ml. Erlenmeyer flask with a reflux tube. The flask was heated on a steam bath for periods of time from 15 minutes to 1 hour. At the end of the heating period the solutions were cooled and analyzed for formaldehyde, using 0.00374 *N* iodine solution, by the method of Donnally (*2*). This consists of adding a small excess of sodium bisulfite solution which contains no excess sulfur dioxide, allowing to stand 15 minutes at room temperature, acidifying the solution to methyl orange, titrating with iodine to remove the excess bisulfite, neutralizing with sodium carbonate solution, and titrating the combined sulfite with iodine.

Table I gives the results obtained.

Table II. Effect of Concentration on Analysis of Mono- and Dimethylol Urea

Concentration, G./L.	% Formaldehyde Observed	
	Monomethylol urea	Dimethylol urea
10	19.8	30.2
6	25.8	43.0
4	29.0	47.0
2	32.8	49.0
0.25	33.2	49.8
0.1	33.2	49.8
0.05	33.3	49.9

At higher concentrations the dimethylol or monomethylol urea forms insoluble substances which cannot be analyzed by this method. Table II gives results of determinations of monomethylol and dimethylol urea at concentrations up to 10 grams per liter and the percentage of formaldehyde observed. For better than 95% accuracy the solutions on heating should be less than 1 gram per liter; for 99% they should be less than 0.2 gram per liter. With undue delay between dissolving the methylol urea and completion of the analysis the amount of formaldehyde available by this method decreases. However, the decrease is usually not observed in less than 24 hours.

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RECEIVED February 21, 1949.

Vacuum Fusion Furnace for Analysis of Gases in Metals

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THE importance of the determination of gases in metals is shown by numerous papers on this subject. Among those who have pioneered in this field are Oberhoffer (*2*) and associates in Aachen, Germany, and Jordan and Eckman (*1*) and others at the National Bureau of Standards in the United States. Numerous additional papers have appeared in which the authors have recognized the importance of furnace design; each in turn has made contributions, but they have been more or less guided by the furnaces described by those who pioneered in this field. In many cases, it has been necessary in this laboratory to carry out analyses on a small quantity of material, and, in view of this, the authors of this paper have made radical changes in furnace design which provide data of maximum precision and reliability. The details of this furnace are shown in Figure 1.

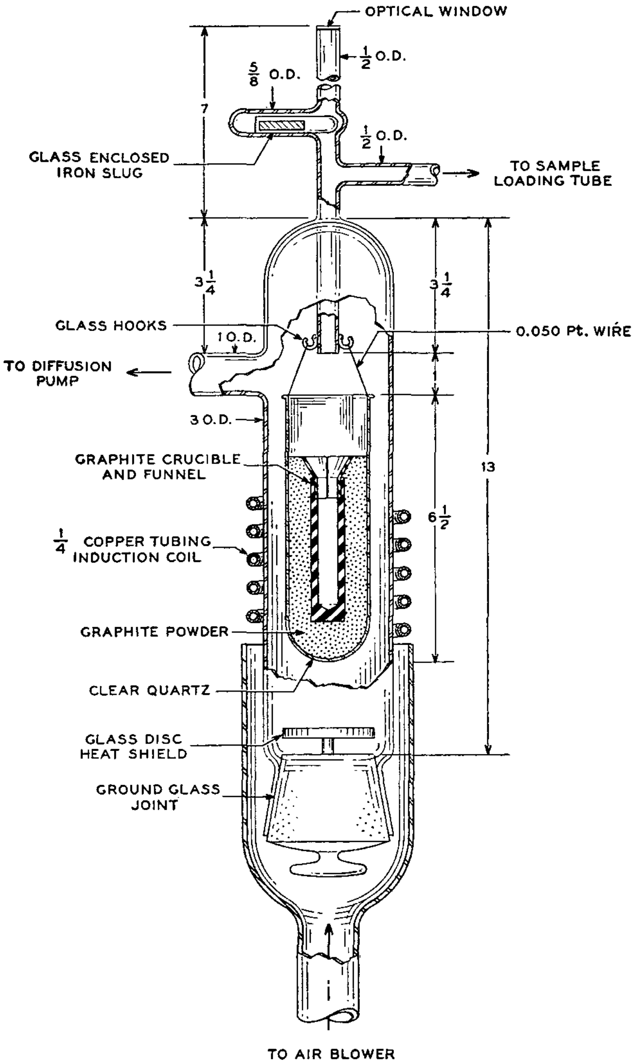

Figure 1

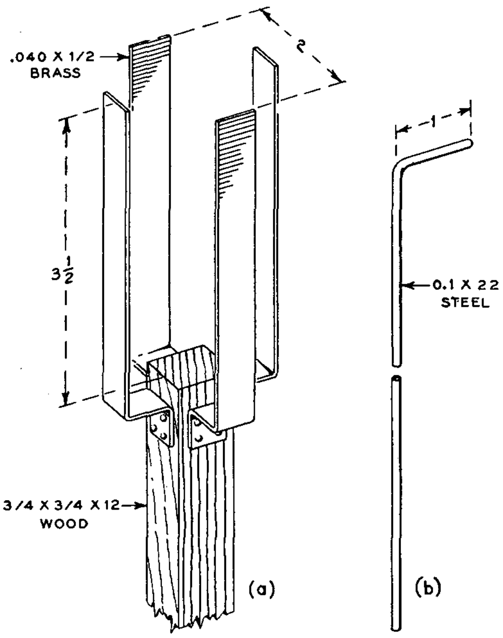

Figure 2

In general, the furnace consists of a glass envelope, a suspended clear quartz tube, and a graphite crucible. The envelope is made of Corning 774 Pyrex and has a removable ground-glass joint at the bottom. This joint is made vacuum-tight by applying a thin coat of sealing wax to the ground surface. The joint is assembled by inserting the wax-coated plug into the female section section. The outer glass surface is then heated with a Bunsen burner and the plug is rotated with pressure until properly seated. The type of wax used is not critical, in that the joint remains cool throughout the furnace operation. Many waxes suitable for vacuum work are available on the market and should be chosen, in part, for their ready solubility in some solvent—for example, no difficulty has been encountered in using Dennison's sealing wax, which is very soluble in acetone. The glass disk attached to the plug acts as a heat shield and provides additional precautions in case of spattering molten metal.

This simple glass design provides a high vacuum envelope which is easy to construct, assemble, dismantle, and clean. A glass flat is shown at the top, through which the temperature can be measured with an optical pyrometer. In order to protect the inner glass surface of the optical flat from becoming coated with metal vaporized from the crucible, a glass-enclosed iron slug is inserted in a side arm, and may be moved back and forth at will by means of a magnet. An additional side arm is provided for admitting the samples to the crucible by means of a magnet. Ten or twelve samples can be readily stored in tubes branching off this side arm. The furnace is sealed by means of the 1-inch glass tube to a two-stage mercury diffusion pump, GHG-10 Special, manufactured by Distillation Products, Inc., Rochester, N. Y. This provides rapid removal of the gases evolved from the molten metal.

A clear quartz tube 2 inches in outside diameter by 6.5 inches is suspended from two glass hooks by 0.050-inch platinum wire. To insert, this tube is placed in the holder shown in Figure 2 and raised into position. The loops of the platinum wire are guided over the glass hooks by means of the bent steel rod. The suspension minimizes the mass of material which will be heated at high temperature. This feature contributes toward obtaining very low blanks on the furnace.

The graphite crucible, 0.75 inch in outside diameter by 0.5 inch in inside diameter by 3 inches, was machined from graphite rod, Grade AGR-National Carbon Company, as shown in the sketch.

A graphite funnel of the same material, split lengthwise to avoid electrical pick-up by the induction coil, is inserted into the end of the crucible. Graphite powder of 200-mesh or less was prepared from the rod with a file.

The quartz tube is filled approximately one third full of graphite powder, the crucible is floated in the powder, and after the top of crucible is covered with a small watch glass, additional graphite powder is added up to the top of the funnel. Every effort should be made to avoid packing the powder about the crucible. A loosely packed assembly results in maximum heat insulation and optimum conditions for out-gassing without danger of lifting the powder from the assembly. The watch glass is removed and any graphite powder within the crucible is blown out, by inserting a small glass tube connected with a rubber hose to a low-pressure air line. The removal of this graphite powder is important, in that the powder in the crucible never reaches the temperature of the crucible during out-gassing and therefore will result in high blanks. Furthermore, the powder will cause a very rapid evolution of gas, which induces undue sputtering of the molten metal.

The furnace is cooled with a high-velocity air stream which is directed uniformly about the walls of the furnace by means of a glass funnel of special design. The air is supplied from a high-speed Breuer Tornado blower which is regulated to the proper speed with a Variac. The elimination of water cooling simplifies the construction and manipulation and reduces the size of the furnace. This reduction of the outside dimensions of the furnace results in the use of a smaller induction coil, and thus provides more efficient heating. The General Electric 5-kw. output unit, which operates at a frequency of approximately 525 kilocycles, will provide ample power. In general, the out-gassing of the crucible is carried out for 2 hours at 2400° C. After this treatment the temperature is lowered to 1650° C.; the amount of oxygen evolved as carbon monoxide in 30 minutes is equivalent to less than 0.0002% oxygen per gram of sample.

This furnace has been in constant use for about 2 years and many determinations have been made on iron, molybdenum-iron alloys, copper, germanium, and nickel. It has been applied to the heating in high vacuum of materials at 2400° C. for continuous periods of 6 hours. The design of the all-glass furnace, providing a high vacuum envelope with full vision, and the suspension of the quartz tube assembly in vacuum eliminate massive metal heads, quartz to metal or glass joints, rubber or lead gaskets, various cements for attaching dissimilar materials, radiation shields, ceramic supports, and water cooling.

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RECEIVED September 20, 1949.

Device for Filtering and Precise Dispensing of Solutions in Closed Systems

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THE use of equipment that assures the complete absence of all forms of foreign matter, such as dust particles, requires special techniques. This is especially true in the high polymer field when light scattering and viscosity measurements are made. A simple device has been constructed for filtering, weighing, and transferring solutions to measuring equipment with a minimum loss of solvent and exposure to the atmosphere. All the parts are readily available and simple to adapt.

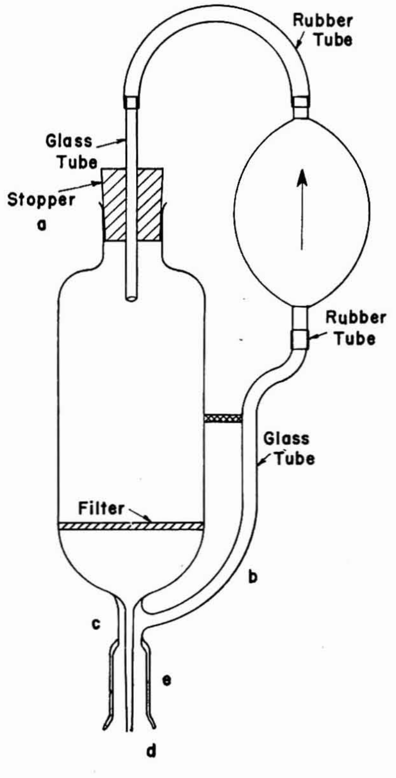

Figure 1. Sintered-Glass Filter

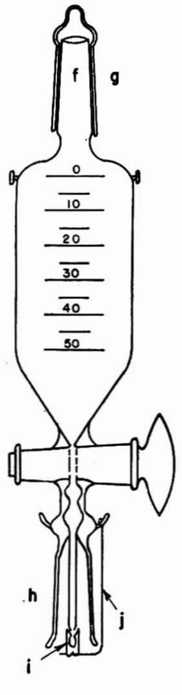

Figure 2. Modified Weight Buret

The device consists of two units, a sintered-glass filter of required porosity and a weight buret. The all-glass filter is constructed as shown in Figure 1. A pressure bulb with valves is placed between *a* and *b* in order to exert pressure on the liquid in the filter bottle, thereby accelerating filtration. In order to eliminate the possibility of liquid being drawn into the tube at *b*, a ring seal *c*, is constructed above the exit tube, *d*. The outer part of a standard-taper ground joint is attached at *e*.

The weight buret is modified as shown in Figure 2. The inner part of the standard-taper ground joint at *e* (Figure 1) is attached to the buret at *f*. This feature permits filtration directly into the buret. A cap, *g*, closes the top of the buret. The outer part of a standard-taper ground joint, *h*, is ring-sealed to the exit tube. In order to prevent loss of liquid while the weighings are performed, the tip of the exit tube is equipped with a small ground-glass cap, *i*, held in place by wire *j*. Evaporation which may occur at the stopcock can be minimized by using a well-ground unit plus a grease not soluble in the solvent used. Sager (*1*) developed tetraethylene citrate for use with aromatic hydrocarbons. The measuring equipment is fitted with the inner part of the standard-taper ground joint at *h*.

When liquids are pipetted from one vessel to another, the chief sources of foreign matter are material clinging to the inner and outer surfaces of the pipet and material drawn into the liquid from the atmosphere. The proper use of the weight buret will permit the transfer of known amounts of liquids with less contamination than results from the use of pipets. The solution can be prepared in the usual manner, and poured directly into the filter bottle, and stopper *a* put in place. If desirable, the stopper may be covered with tin foil to avoid possible contamination or the unit can be replaced by a standard-taper glass joint. With the filter unit and buret connected, the filtered liquid will enter the buret more rapidly if pressure is exerted with the rubber bulb. The buret is then removed, capped, and weighed before liquid is transferred to the measuring equipment.

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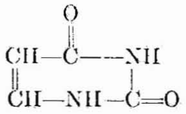
RECEIVED April 16, 1949.

CRYSTALLOGRAPHIC DATA

27. Uracil (2,6-Dioxypyrimidine)

Contributed by VICTOR GILPIN[1] AND WALTER C. MCCRONE, Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill.



Structural Formula for Uracil

Uracil is difficultly soluble in all solvents, but can be recrystallized from ammonium hydroxide by evaporation of ammonia either by cooling or by addition of hydrochloric acid. The crystals are not, however, well formed nor were the very small crystals obtained from pyridine, alcohol, benzene, or acetone any better. The only good crystals ever observed were formed by slow sublimation; those for x-ray diffraction were formed overnight in a Kofler sublimation block at 300° C. (Figure 2,*a*); those used for optical studies were obtained by sublimation from one microscope slide to a second supported just above the first slide (Figure 2,*b*).

The latter arrangement worked so well that it is worth describing in detail.

A sheet metal band about 7 inches long was bent to pass completely around the long direction of the two slides lying parallel to each other. The two slides were held by the metal band so that two ends were in contact with a wedge-shaped opening between them 0.125 inch wide at the open end. About 100 mg. of uracil were then placed between the two slides in the narrow part of the wedge. Heat was applied, using an alcohol lamp or equivalent so that the thin end becomes hottest; however, no effort was made to keep the rest of the assembly cool. In fact, the largest and best crystals will be formed if the top slide is very hot and only a few degrees below that of the bottom slide.

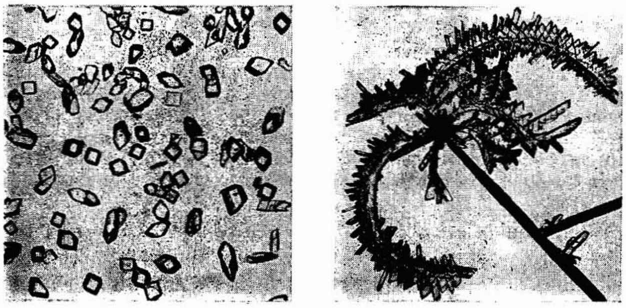


Figure 1. Uracil Sublimate

No evidence of polymorphism has been observed.

CRYSTAL MORPHOLOGY

Crystal System. Monoclinic.

Form and Habit. Equant crystals lying on $\bar{3}01$ or elongated parallel to c lying on 100, 010, or 110. The following forms are shown: clinopinacoid {010}, orthopinacoid {100}, positive hemiorthodome {$\bar{3}01$}, and prism {110}.

Axial Ratio. $a:b:c = 0.921:1:0.293$.

Interfacial Angles (Polar). $110 \wedge \bar{1}10 = 100°$.

Beta Angle. 113°.

Twinning Plane. 100.

Cleavage. $\bar{3}01$.

X-RAY DIFFRACTION DATA

Cell Dimensions. $a = 11.4$ A.; $b = 12.38$ A.; $c = 3.63$ A.

Formula Weights per Cell. 4.

Formula Weight. 112.09.

Density. 1.625 (flotation); 1.590 (x-ray).

Principal Lines

d	I/I_0	d	I/I_0
7.88	0.27	2.40	0.08
5.30	0.32	2.31	0.06
5.10	0.32	2.20	Very weak
4.71	0.10	2.09	Very weak
3.62	0.21	2.02	Very weak
3.44	0.15	1.96	Very weak
3.21	Very weak	1.89	Very weak
3.14	1.00	1.76	Very weak
2.81	0.10	1.71	Very weak
2.73	0.08	1.68	Very weak
2.64	Very weak	1.60	Very weak
2.56	0.14	1.56	Very weak
2.50	Very weak	1.44	Very weak

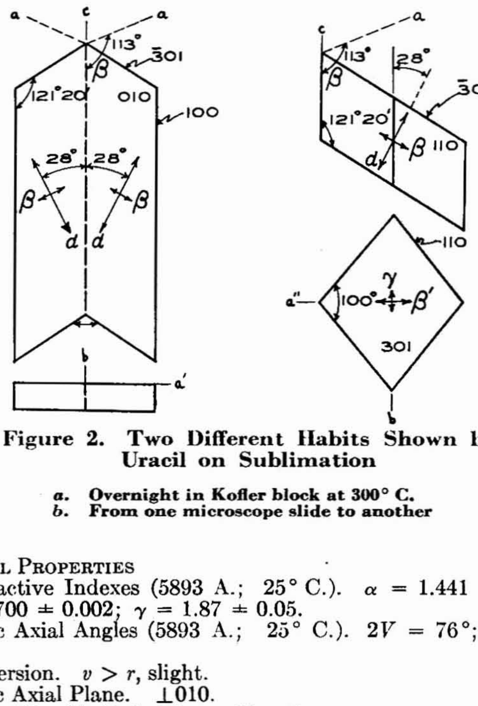


Figure 2. Two Different Habits Shown by Uracil on Sublimation

a. **Overnight in Kofler block at 300° C.**
b. **From one microscope slide to another**

OPTICAL PROPERTIES

Refractive Indexes (5893 A.; 25° C.). $\alpha = 1.441 \pm 0.002$; $\beta = 1.700 \pm 0.002$; $\gamma = 1.87 \pm 0.05$.

Optic Axial Angles (5893 A.; 25° C.). $2V = 76°$; $2H = 87°$.

Dispersion. $v > r$, slight.

Optic Axial Plane. $\perp 010$.

Sign of Double Refraction. Negative.

Optical Orientation. $Bx_0 = \gamma = b$; $\alpha \wedge c = 27.5°$ in acute β.

Molecular Refraction (R) (5893 A.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.661$. R (calcd.) = 25.2. R (obsd.) = 26.5.

FUSION DATA

Uracil melts with sublimation and decomposition at 338° C. The microscopic preparation, if cooled immediately, will show many well-formed crystals, resulting from sublimation, and a brown glass made up of partly decomposed supercooled melt. The crystals may lie on 001, 110, or 010. They show twinning on 100 and cleavage parallel to $\bar{3}01$.

CONTRIBUTIONS of crystallographic data for this section should be sent to Walter C. McCrone, supervisor, Analytical Section, Armour Research Foundation of the Illinois Institute of Technology, Chicago, Ill.

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BOOK REVIEWS

Modern Methods for the Analysis of Aluminum Alloys. *G. H. Osborn* and *W. Stross*, editors. vii + 144 pages. Chapman & Hall, Ltd., 37 Essex St., London W.C.2, 1949. Price, 13s. 6d.

This book is somewhat unusual, in that it gives the experienced analyst the latest procedure for rapid analysis and at the same time shows the inexperienced technician how to make accurate determinations without becoming confused with irrelevant material.

The book is especially recommended for use by the busy chemist in the small laboratory, who is supposed to perform miracles with little equipment and little or no help.

The short paragraph on sampling and the confinement of the work to elements related directly to aluminum alloys actually in production gives the book a practical aspect not found in similar works.

ARTHUR BIDDLE

Colorimetric Methods of Analysis. *Foster Dee Snell* and *Cornelia T. Snell.* Vol. II. 3rd ed. x + 950 pages. D. Van Nostrand Co., Inc., 250 Fourth Ave., New York 3, N. Y., 1949. Price, $12.

The present Volume II is a completely rewritten and expanded version of the material on inorganic analysis found in Volume I of the second edition, and the revision appears to be complete through 1947. To quote from the preface, the book is a "selected collection of available methods" and will save time in "avoiding the necessity of reference to a complete library."

In general, each chapter contains an opening section on the occurrence of the element in question, followed by directions for the preparation of various types of material for analysis. The chapter is then concluded with directions for the determination. Presentation of the material sometimes lacks continuity; one may occasionally wonder which method of sample preparation is suitable for what method of determination if not familiar with the subject matter. Occasional difficulties may be encountered through errors in directions of the type on page 206, which instruct to "heat to fumes of sulfur trioxide" (lines 12 and 13) but neglect to include the addition of this acid (lines 4 and 5). Curves illustrating the absorption characteristics of the various compounds are conspicuous by their absence, the one example on page 443 being illustrative of the type of information the analyst will find desirable.

The above criticisms will not detract from the over-all utility and value of the book as a reference manual. The voluminous and repetitive literature of more than a decade since the previous edition has made the task of selection and coordination a difficult one, and the analyst will feel gratified to find so much useful material gathered in one place.

JOHN L. HAGUE

North Jersey Meeting-in-Miniature

THE scientific groups of the North Jersey Section, AMERICAN CHEMICAL SOCIETY, held a meeting-in-miniature at Newark on January 9, at which papers were presented before the Analytical, Industrial Engineering, Organic, and Polymer Groups. Abstracts of the papers presented before the Analytical Group are presented below.

Sodium and Potassium Determination in Refractory Materials Using the Flame Photometer. FRANK M. BIFFEN, Johns-Manville Research Center, Manville, N. J.

A method has been devised by which refractory materials are sintered with calcium carbonate as in the J. Lawrence Smith method, and sodium and potassium are determined on the water extract using the flame photometer. Consideration is given to the calcium present in the extract. Results obtained by this method appear to be at least as accurate as, and probably more accurate than, those obtained using the J. Lawrence Smith method, and the time necessary to complete the analysis is cut in half.

Determination of Sodium and Potassium, Employing Ion Exchange Separation. JOHN BEUKENKAMP AND WILLIAM RIEMAN III, Rutgers University, New Brunswick, N. J.

An accurate method for determining sodium and potassium, employing ion exchange as a means of separation, was proposed. The method and results of separating sodium, potassium, and magnesium from mixtures of the three with subsequent determination of the sodium and potassium were given. Some elution variables and theoretical aspects were also considered.

Conductometric Titration of Amino Acids. N. HOWELL FURMAN, Princeton University, Princeton, N. J., GEORGE H. MORRISON, Rutgers University, New Brunswick, N. J., AND ARTHUR F. WAGNER, Princeton University, Princeton, N. J.

In the past, conductometric titrations have had limited application in study of proteins, but the investigation of amino acids by this technique has been almost completely deferred. In the latter case one is concerned with ampholytes and consequently direct conductometric titration of the amino group leads to very unsatisfactory results.

It was proposed by Loiseleur and Lesage [*Compt. rend.*, **218**, 969 (1944); **221**, 136 (1945)] that amino acids could be determined by conductometric titration if an excess of standard hydrochloric acid was first added, followed by back-titration with sodium hydroxide. They interpreted the titration graph of glycine as being composed of a branch due to the excess of acid followed by titration of the $—NH_3^+$ group and then titration of the carboxyl group.

A rather extensive study by the authors of the behavior of amino acids of the acidic, basic, and neutral types has led to a more satisfactory theoretical interpretation of the conductometric titration of these acids and their mixtures.

The titration curves are best interpreted as a neutralization of free hydrochloric acid plus carboxyl group, which in many cases gives a rapidly falling branch that is almost linear. This branch is followed by neutralization of a $—NH_3^+$ group. The detailed behavior is readily explainable on the basis of the known ionization constants of the various acids and the formation of dipolar ions, which accounts for the very rapid drop in conduction during the titration of the carboxyl function.

Because all the studies were concerned with acids in which the amino group was α to the carboxyl, it was felt that an examination of several compounds in which the functional groups were further removed from each other might provide interesting results. An examination of the ortho, meta, and para isomers of aminobenzoic acid as well as β-alanine further substantiated this interpretation.

An examination of the effect of various acids and salts on the slopes of the conductivity curves was performed in an attempt to determine the most effective acid to be added in excess prior to the titration. Similarly, the effect of semiorganic solvent mediums on the slopes of the curves was examined. Amino acids with additional functional groups such as the sulfhydryl group of cysteine produced titration curves that conformed to the authors' explanation of the proper sequence of the titration steps. It is thus believed that a better theoretical interpretation has been presented of the conductometric titration of amino acids and their mixtures.

Chemical Determination of Calcium Pantothenate. C. R. SZALKOWSKI, W. J. MADER, AND H. A. FREDIANI, Merck & Co., Inc., Rahway, N. J.

Calcium pantothenate is one of the essential ingredients added to many vitamin preparations and enrichment mixtures. A method for its accurate determination is, therefore, a matter of considerable importance in vitamin analysis; however, no chemical method has been proposed hitherto.

Hydrolytic cleavage of pantothenic acid in alkaline or acid media results in the formation of β-alanine and α,α-dihydroxy-$\beta,$-β-dimethylbutyric acid. β-Alanine when treated with potassium permanganate in the presence of potassium bromide under properly regulated conditions yields an insoluble compound upon treatment with 2,4-dinitrophenylhydrazine. The ratio between the amount of this product and the hydrolyzed pantothenate oxidized is constant and can be estimated by dissolving the dinitrophenylhydrazone in pyridine, diluting with sodium hydroxide, and measuring the resulting blue color spectrophotometrically at 570 millimicrons. Beer's law is followed over a suitable concentration range.

Interference from niacin, niacinamide, thiamine, vitamin B_6, and soybean flour is removed by chromatographing the aqueous solution of the sample on aluminum oxide columns. Ascorbic acid, however, interferes and has not been successfully removed chromatographically as yet.

Multicomponent Spectrophotometry. Method of Improving Precision in Two-Component Analysis.

EUGENE ALLEN AND ELLWOOD M. HAMMAKER, Rutgers University, New Brunswick, N. J.

In the first paper of this series (presented at the September 1949 meeting of the AMERICAN CHEMICAL SOCIETY in Atlantic City), the precision of the conventional spectrophotometric determination of components *m* in a mixture of two light-absorbing materials *m* and *n* was discussed mathematically. The present work has shown that this precision can be improved considerably by placing a solution of *n* (the component that is not being determined) in the reference cell instead of pure solvent. The concentration of the solution of *n* need not be known exactly, and no change is made in the method of calculating the results.

Putting *n* in the reference cell will have the same effect as taking *n* out of the sample cell. Obviously, the value obtained for the concentration of component *m* will not be affected by any change in the concentration of *n* in the sample solution. Therefore, the use of a reference solution of *n* will not affect the accuracy of the results obtained.

However, there will be a considerable effect on the precision. It can be demonstrated that: (1) for a given solution of *m* and *n*, to be analyzed for *m*, the higher the concentration of *n* in the reference solution, the greater the precision; (2) when the concentration of *n* in the reference solution has reached a point where it cannot be further increased (100% transmittance reading at one of the two wave lengths used), a still further gain in precision can be obtained by increasing the concentrations of both the sample and the reference solutions to the same degree, up to a certain optimum value which can be calculated. (In practice, this optimum value may possibly not be reached because the limit of widening of the slit may occur beforehand, as the concentrations of the solutions are increased.)

The method is universally applicable for determination of one component in two-component systems, provided that the following conditions are met: Beer's law must be followed; and the absorbances of the solutions must not change appreciably with change in slit width. The latter requirement arises from the fact that the slit width of the spectrophotometer must be widened when a reference solution is used, to compensate for the light lost by absorption in the reference solution.

To test the method, mixtures of potassium phthalate and potassium chromate were analyzed for potassium phthalate by means of a Beckman spectrophotometer, both by the conventional procedure and with the use of a reference solution of potassium chromate. It was shown that by the latter procedure the standard deviation of the value obtained for the phthalate concentration can be reduced to considerably less than the usual figure, and this simple expedient introduces no complications in the analysis. The change in standard deviation found is close to that calculated from the theory.

The Decomposition of Potassium Iodate during the Baking of Bread.

J. B. CONN, C. M. HOLLENBECK, D. T. WOODBURY, AND C. ROSENBLUM, Merck & Co., Inc., Rahway, N. J.

Small amounts of potassium iodate added to bread dough improve the handling qualities of the dough. The fate of this salt during the bread-baking process is difficult to determine by standard analytical procedures because of reactions occurring during the extraction process prior to analysis. An attempt was made to solve the problem by means of iodate prepared from radioactive iodine (I^{131}).

Bread was baked with radioactive potassium iodate (2 mg. per loaf) of known specific activity (counts per minute per mg.) and samples were extracted with ammoniacal methanol. To minimize reaction of iodate and iodide with small amounts of reducing material extracted simultaneously, 100 to 200 mg. each of inert potassium iodide and iodate were added at the time of extraction. The addition of those inert carriers had the advantage of facilitating subsequent separation of components. Iodide and iodate were precipitated as silver salts, and the silver iodate was washed out with aqueous ammonia. The filtrate containing the iodate was treated with sulfurous acid and acidified to produce a second silver iodide precipitate representing the original iodate. The formation and washing of precipitates were performed for the most part in centrifuge tubes, no attempt being made at purification because of the difficulty of removing certain mucilaginous impurities. In any case, purification was unnecessary because the radioactivity, and not the weight, of a component was being determined.

Both precipitates were dissolved in cyanide solution and made up to volume, and their radioactivity was determined by means of a thin-window Geiger-Müller counter. Self-absorption and decay corrections were made where necessary. The activity of extracted fat, residual solids, and off-gases released during the baking was also determined. The efficiency of the separation procedure was ascertained in separate experiments with radioactive iodate and iodide dissolved in ammoniacal methanol extracts of bread baked without radioactive iodate. These tests revealed the necessity of adding inert carrier to swamp out reactions occurring during the extraction, when only minute amounts of iodine-containing salts are involved.

By comparing the radioactivities (in counts per minute) of the several fractions, which reveals unequivocally the distribution of the original radioactive iodine, it was concluded that a maximum of 7.5% of the original iodate remained unchanged, about 90% appeared in the form of iodide, and the remainder distributed between the fat fractions and residual solids. The latter probably represent incomplete separation of salts rather than iodinated compounds. No significant volatilization of iodine-containing compounds occurred.

Freezing Points in the Determination of Product Purity.

C. R. WITSCHONKE, American Cyanamid Co., Calco Chemical Division, Bound Brook, N. J.

The measurement of time-temperature freezing and melting curves is one of the most generally useful methods known for accurately determining the purity of relatively pure materials. Recent advances in the construction of rugged, yet sensitive, resistance thermometers and automatic temperature-recording instruments should pave the way for more general use of this method in industrial measurement and control of product purity. The paper briefly outlined the scope of the freezing point method and described some new developments.

The mole fraction purity, X_1, of an impure material is related exactly to the freezing point of the mixture, T_f, on the absolute temperature scale by the relation:

$$-\ln X_1 = \frac{L_f}{RT_0} \frac{(T_0 - T_f)}{T_f} \tag{1}$$

when all the impurities are soluble in the melt and form ideal mixtures with the major component. L_f and T_0 are the molar heat of fusion and freezing point, respectively, for 100% pure material.

Generally L_f is known or can at least be estimated with sufficient accuracy from values for similar compounds by application of Walden's rule that L_f/T_0 = constant. T_0 can be determined from a sample which is not necessarily 100% pure by determining the freezing point lowering when a definite fraction of the sample has frozen. The conversion from mole fraction purity to weight fraction purity depends on a knowledge of the approximate molecular weights of the impurities.

A large number of organic systems are ideal or so nearly so that Equation 1 can be used to determine entire freezing point diagrams, including eutectic temperatures and compositions. A few examples were given. Thus, for isomeric or other nearly ideal systems, Equation 1 can be used to analyze products even though impurity concentrations become high.

For nonideal systems, two possibilities are dealt with. In the first, the average molecular weight and deviation from ideality of the impurities remain relatively constant, so only a few measurements of synthetic mixtures are necessary to determine a calibration curve accurately. In the second, for which the average molecular weight and deviations from ideality of the impurities vary widely, a two-solvent method is often effective in analyzing for the component of interest.

The following methods of measurement of freezing point curves were discussed, including advantages and disadvantages of each: classical method in general industrial usage; constant, large temperature differential method in use at National Bureau of Standards; constant, small temperature differential method in use at Calco; and automatic equipment and platinum resistance thermometry.

Analysis of Pyrazine. Assay and Determination of Basic Impurities. WILLIAM SEAMAN, J. T. WOODS, AND WLADIMIR LEIBMANN, American Cyanamid Co., Calco Chemical Division, Bound Brook, N. J.

A method proposed for the determination of pyrazine involves the formation of an insoluble mercuric sulfate addition compound by reaction with a known volume of standard mercuric sulfate in excess. The insoluble mercury complex is filtered off and the excess mercury is determined by the Volhard method. The precision of the proposed method, expressed as the standard deviation, is ±0.25% (absolute). Piperazine, diethylenetriamine, ethylenediamine, and ethanolamine do not interfere, provided that the precautions suggested are followed. Coprecipitation of some of the impurities present may take place if the precipitant is added too rapidly or if the sample is added to the precipitant. A small correction is applied for the solubility of the mercury complex.

Some indication of the amount of the above-mentioned basic impurities is obtained from a potentiometric titration of the sample with standard alkali after adding an excess of standard acid. In general two inflection points are obtained, at about pH 4 and 8. From the volume of the standard alkali consumed to each of these breaks, and from the amount of acid added, it is possible to obtain some information in regard to the amount and type of basic substances which are present as impurities.

The water in the sample may be determined by means of Karl Fischer reagent in the usual manner.

Delaware Chemical Symposium

THE Delaware Section of the AMERICAN CHEMICAL SOCIETY in collaboration with the University of Delaware sponsored the second Delaware Chemical Symposium on the University of Delaware campus at Newark, January 21. Section meetings were held on analytical, organic, physical, and polymer chemistry, in addition to a program of papers on chemical development and applications research. Abstracts of the papers presented before the analytical chemistry section are printed here.

Determination of Small Concentrations of Carbonyl Compounds by Differential pH Method. H. R. ROE, Polychemicals Department, Du Pont Experimental Station.

Aldehydes and ketones react with hydroxylamine hydrochloride forming oximes and liberating hydrochloric acid. Under selected conditions, the decrease in pH, resulting from the release of hydrochloric acid, is a direct measure of the concentration of carbonyl compounds present. A rapid routine method was described which includes the calibration of a standard working curve under optimum conditions for this reaction at carbonyl concentrations of 0.01 to 0.1%, from which a direct quantitative determination of carbonyl can be made by simple pH measurements. The method has been found generally applicable to aldehydes and methyl ketones. The time required for a single analysis is about 5 minutes. Results are reproducible to ±2% relative.

Polarographic Estimation of Formaldehyde. GEORGE A. CROWE AND CECIL C. LYNCH, University of Delaware.

The influence of pH, temperature, and supporting electrolytes on the polarographic wave height of formaldehyde has been studied over the range of pH 8.77 to 12.7, and from 15° to 95° C. By the Arrhenius equation it is possible to estimate the dehydration of formaldehyde in dilute aqueous solutions from polarographic wave height on the assumption that this wave height depends upon the dehydration rate of a formaldehyde hydrate at the dropping mercury electrode.

Microdetermination of Sulfur by the Grote Method. Photometric Detection of Titrimetric End Point. ROLAND N. WALTER, Hercules Experiment Station.

In the Grote combustion micromethod for determining sulfur in organic compounds, the sulfate formed is usually titrated with standard barium chloride solution, using tetrahydroxyquinone or an alkali salt of rhodizonic acid as an internal indicator. A photometric method of detecting the end point, which is more objective than the usual visual method, was described. Titration results are reproducible within 0.004 mg. of sulfur.

Use of Iodine Reagents for Determination of Purity and Water Content of Xanthates and Dithiocarbamates. A. L. LINCH, Miscellaneous Intermediates Area Laboratory, Du Pont Chambers Works.

The reaction of iodine with salts of xanthates and dithiocarbamates to produce the disulfide derivatives by oxidation is old and familiar chemistry, but its application to the estimation of purity has encountered interferences. Best results have been obtained by conducting the iodometric titrations in alcohol as a solvent, and using the conventional starch solution as an outside indicator. Good agreement with purity derived from sulfur (Parr bomb) and nitrogen (Kjeldahl) content was attained.

Application of the Karl Fischer reagent for moisture has furnished a method for the accurate determination of water of hydration as well as extraneous moisture in crystalline xanthates and dithiocarbamates. In view of the ease with which these derivatives are oxidized to the disulfide in aqueous systems, the preferential reaction of the Fischer reagent iodine with the water without further reaction with the sulfhydryl groups in the anhydrous system was unexpected, and indicates that the iodine may be present in the reagent as a complex rather than as a simple solution. Twenty xanthate derivatives and fourteen nitrogen-substituted dithiocarbamates were investigated in the course of this study to establish limits for these iodometric procedures.

Determination of Trace Amounts of Chlorine in Organic Compounds. WILLIAM H. CALKINS, Polychemicals Department, Du Pont Experimental Station.

A method has been developed for the determination of trace amounts of chlorine in organic compounds with an accuracy and precision of ±1 p.p.m. in the range of 0 to 10,000 p.p.m. of chlorine. It is based on the combustion of a large sample followed by scrubbing of the off-gas and potentiometric titration of the scrubber solutions.

The procedure has been shown to be applicable to adiponitrile, benzene, cyclohexane, and methanol. No difficulty is anticipated in application to other combustible organic compounds. Solids may be analyzed by dissolving them in solvents which have been so analyzed, and combustible gases may be analyzed merely by metering known amounts into the apparatus.

L.S.U. Analytical Symposium

THE third annual Symposium on Modern Methods of Analytical Chemistry was held on the campus of the Louisiana State University, Baton Rouge, La., January 30 to February 2. Abstracts of papers presented are reproduced here.

Polarography. PAUL DELAHAY, Louisiana State University, Baton Rouge, La.

Introduction
Instrumentation
1. Measurement of the diffusion current
    - Photographic recording instruments
    - Pen-and-ink recording instruments
    - Manual method
2. Differential methods
    - Method involving two dropping mercury electrodes
    - Method involving superposition of an alternating voltage
3. Special methods for investigation of reversibility-irreversibility character of an electrode reaction
    - Kalousek's method
    - Oscillographic methods

Recent Advances in Theory
- Investigation of validity of Ilkovič equation
- Equation of wave for an irreversible electrode reaction
- Comparison of half-wave potentials with potentials calculated from thermodynamic data
- Limiting current controlled by reaction rate
- Adsorption waves

Present Trend in Polarographic Research

1. Supporting electrolyte
    - New supporting electrolytes
    - Organic media
    - Fused salts
2. Electrodes
    - Use of solid microelectrodes
3. Auxiliary techniques
    - Electrolytic separation
    - Concentration by electrolytic deposition and redissolution
    - Use of organic reagents
4. Applications of polarograph as analytical tool in research and industrial control
5. Applications to study of properties of certain compounds

Oscillographic Polarography
- Principle of the Method
- Instrumentation
    - Single-sweep method of recording
    - Multisweep method of recording
- Characteristic Features of Oscillographic Wave
    - Shape of wave
    - Randles-Sevcik equation and comparison with Ilkovič equation
    - Influence of rate of electrode reaction
    - Influence of capacity current
- Comparison with Ordinary Method and Conclusion

Use of the Microscope in Analysis. W. C. McCrone, Armour Research Foundation, Illinois Institute of Technology, Chicago, Ill.

Analysis is interpreted to include determination of those physical properties useful in characterizing or identifying a material (color, crystal shape, crystal optics, molecular weight, refractive index, melting point, etc.) which can be determined microscopically. It includes as well the determination of purity and both qualitative and quantitative methods.

1. Morphological Methods
    - Natural products
        - Plant materials, fibers, starches, pollens, foods
        - Animal materials, tissues, bacteria
    - Minerals
        - Gems, abrasives
    - Metals
    - Miscellaneous
        - Dust, dyes, pigments
        - Formation of characteristic precipitates of inorganic, organic, or metallic materials by addition of specific reagents
        - Crystallization of typical crystals of fusible materials from melt
2. Qualitative Methods
    - Areal analysis
        - Metals, amatols
        - Porosity of filters
        - Plastic mounts of solid particulate mixtures
    - Counting analyses
        - Fibers
        - Particles
    - Rate of crystal growth
    - Crystal optics
        - Isomorphous mixtures
        - Change in refractive indexes, optic axial angle, etc.
    - Refractive index of melt
3. Crystallographic Methods
    - Crystal geometry
        - Habit
        - Profile angles
        - Interfacial angles
        - Axial ratios
    - Crystal optics
        - Color and pleochroism
        - Refractive indexes
        - Sign of double refraction
        - Dispersion ($v > r$, $v > r$)
        - Interference figure
    - Correlation of optics and geometry
        - Extinction
        - Optic axial plane
        - Acute bisectrix
        - Dispersion
        - Crossed, horizontal, inclined
4. Fusion Methods
    - Characterization of fusible materials
        - Sublimate
            - Appearance and optics
            - Rate of crystal growth from melt
            - Type of crystal growth from melt
            - Profile angles, extinction, birefringence, refractive indexes relative to melt, interference figure
            - Polymorphism
            - Mixed fusion with thymol
            - Profile angles, extinction, birefringence, refractive indexes relative to melt, interference figure
        - Micromelting point
            - Simple compounds
            - Eutectics with known second components
            - Molecular weight determination
        - Refractive index of melt
        - Purity

Organic Reagents. John F. Flagg, Knolls Atomic Power Laboratory, Schenectady, N. Y.

Quantitative Precipitations. The role of pH in affecting the selectivity of organic reagents as applied in precipitation analysis has been recognized for some time. In general, most organic precipitants function in a more specific manner at lower pH values than at higher ones. Comparatively few organic precipitants may be used in strongly acidic solution, but those that may are selective in their action.

It is possible to describe quantitatively the role of the hydrogen ion concentration and the metal ion concentration in such precipitations, and to obtain solubility product constants for the various metal chelates with which one deals. Applying these solubility product constants under conditions of known reagent concentration and estimated metal ion concentration, it becomes possible to predict the pH ranges for separations of various metallic ions with a given reagent. In certain cases it becomes possible only to make group separations, as in the case of hydrogen sulfide precipitations.

The usefulness of organic reagents as precipitants will be greatly increased as additional data on solubility products are available.

Partition Equilibria. Many chelate compounds, such as those formed by the interaction of a metallic ion and an organic reagent, are highly soluble in organic solvents of the polar type and may thus be removed from aqueous solution by extraction procedures. Numerous factors affect the extractability, including the pH of the aqueous phase, the concentration of reagent used, the valence of the metallic ion, and the solubility and dissociation relations of the species involved. As different metallic ions will form chelates of differing degrees of stability towards acid, and extractability, it becomes possible to make analytical separations by extraction in a rather selective manner.

In addition to the usefulness of organic reagents in performing separations of this type, much information can be obtained in the study of ionic species in solution, particularly those formed by ion association reactions. Certain new organic reagents provide powerful tools for attacking problems of this sort.

Inorganic Fluorometric Analysis. Charles E. White, University of Maryland, College Park, Md.

General Concepts, Literature, Apparatus. Fluorescence is classified under the general phenomenon of luminescence and depends upon immediate excitation. Cathode rays, alpha-particles, and ultraviolet light are the usual sources of exciting energy. The ultraviolet rays are obtained from electric arcs, mercury vapor lamps, or suitable phosphors. Fluorescent spectra may be somewhat correlated with the absorption band of the substance concerned.

There is much important literature on fluorescence and a library on this subject is readily established.

The apparatus necessary for the fluorescence laboratory is relatively simple and consists of visual as well as photoelectric instruments. Fluorescent microscopy involves the adaptation of an ordinary microscope to this form of analysis.

Applications of fluorometric analysis may be found in all branches of chemistry.

Quantitative Inorganic Applications. Fluorometric procedures for the analysis of aluminum, beryllium, boron, lithium, zinc, uranium, gallium, and iodine are well developed from a quantitative standpoint.

A brief outline of the method, typical results, the nature of the complex formed, and possible applications was given for each of these elements.

Qualitative Applications. Fluorometric techniques are no more difficult than usual colorimetric procedures and are of considerable use in the ordinary scheme of qualitative analysis. Fluorescent tests have been developed for sodium, aluminum, zinc, boron, thorium, ammonia, thallium, antimony, uranium, mercury, and oxygen. With suitable reagents many of these may be identified in the presence of similar elements. Bead test, spot test, paper, and the usual solution tests are applicable.

Fluorescent methods are important in the identification of minerals and ores.

Infrared Spectroscopy in Chemical Research and Analysis. NORMAN WRIGHT, Dow Chemical Co., Midland, Mich.

I. Infrared Spectroscopy, an Established Method
  A. Development during the past decade
  B. Modern commercial spectrophotometers
  C. Extent of present-day applications
II. Capabilities of Method
  A. Qualitative and structure analysis
    1. Fingerprint method, use of punch cards
    2. Bands characteristic of groups
    3. Use of polarized radiation
  B. Quantitative analysis
    1. Scanning methods *vs.* stationary settings
    2. Differential methods, matched cells, and use of double-beam optics
  C. Application to inorganic compounds
  D. Continuous type infrared analyzers
III. Future Trends in Utilization of the Method
  A. As a tool for analysis, plant production control, quality control, product specifications, etc.
  B. As a tool for research, closer liaison between chemist and spectroscopist

Profile Angles in Analytical Chemical Microscopy. A. C. SHEAD, University of Oklahoma, Norman, Okla.

Definition of Profile Angle. The interfacial angle of crystallography or its projection

Use of Profile Angle. A constant like a melting or boiling point. The law of constancy of interfacial angles in the form of a corollary involving a function, applies. This constant is used in the identification of substances

Field of Application. To flat, tabular crystals extended in two directions but of restricted development in the third

Method of Orientation. By gravity

Advantages. Simplicity of geometrical form and demonstrable differences in angular magnitudes on these forms are appreciable by laymen. Reduction of classical crystallography to a single plant simplifies operations for professionals. Measurement of profile angles is simple.

Profile Angles. Angles on substances that always assume the same crystal shape

Compatible Angles. Angles derived from profile angles by calculation or geometrical projection, or reducible to the profile angle by such methods

Formation of Crystals Suitable for Profile Angle Measurement
  Crystallization from solutions
  Crystallization by sublimation
  Crystallization from melts

Rate of crystallization must be slow enough to avoid colloidal condition but rapid enough to avoid complex crystal formation.

Sources of Confusion.
  Amorphous condition
  Polymorphism. Simultaneous appearance of polymorphs
  Pseudomorphs

Illustration by Photomicrographs

Analytical Chemistry in Quality Control of Product and in Research. B. L. CLARKE, Merck & Co., Inc., Rahway, N. J.

A description of the similarities and contrasts in the role of the analytical chemist in two types of industry—the research and development branch of a large electrical communications industry, and a typical chemical industry with emphasis on drugs and fine chemicals.

In each case an analysis was given of why analytical chemists and analytical chemistry are needed, followed by descriptions of the evolution of analytical and control organizations to fit these needs. The various specialized groups were described and finally an appraisal was offered of what the analytical chemist is able to contribute to the types of industrial organizations considered.

Especial emphasis was placed on the use of statistical methods in connection with analytical and control organizations. It was also pointed out that there are many different types of work for people basically trained in analytical chemistry for which industry has a need.

Colorimetric Analysis with Organic Reagents. JOHN H. YOE, University of Virginia, Charlottesville, Va.

About 2000 years ago Pliny developed a test for iron in vinegar. The reagent was simply a piece of papyrus soaked in a solution of gallnuts; when dipped in vinegar it turned dark blue or black if iron was present. This seems to be the first chemical reagent on record, and although now twenty centuries old, it is still used in vinegar works for the detection of iron in vinegar, though filter paper, rags, or wood shavings have replaced the ancient papyrus. Thus the oldest recorded test for a chemical element involved the use of an organic reagent (gallnut) supported by an organic substance (papyrus). The ancient Greeks and Romans detected the presence of alkali in natural waters by its decoloration of red wine. Thus organic reagents were used in making colorimetric analyses centuries before chemistry developed into a science. Unfortunately, however, comparatively few chemists have seemed to realize the advantages and possibilities of organic compounds not only as colorimetric reagents but also in gravimetric and nephelometric analysis. The tendency towards specialization has limited more and more the number of those who are trained both in organic and in analytical chemistry, not to mention the various ramifications in the fields of inorganic and physical chemistry. Perhaps this explains in part at least, why there has been, until comparatively recent years, such a lag in research in the field of organic analytical reagents. The vast number and great variety of organic compounds offer one of the most promising sources for new and better colorimetric reagents, ones that are specific or selective, and highly sensitive.

The problems involved in a thorough investigation of a new colorimetric reaction were outlined and some of the more recently developed colorimetric methods employing organic reagents were used as examples. It was emphasized that much experimental work is still needed to establish a better knowledge of the relationships between the molecular structures of organic compounds and their reactions with inorganic ions. When a new reaction is discovered which looks promising from the standpoint of colorimetric analysis, it is then necessary to make a thorough investigation to determine the nature of the reaction, its stability to light and to atmospheric conditions, its sensitivity, selectivity, optimum conditions for its use, the interference of various ions, and its application to the analysis of standard samples. Continued search among the vast number and many types of organic compounds will undoubtedly yield new and better colorimetric reagents.

The Analyst's Calendar

Determination of Tetraethyllead in Gasoline

A Symposium on Recent Developments in Instrumental Methods for the Determination of Tetraethyllead in Gasoline will be given by Research Division III on Elemental Analysis of A.S. T.M. Committee D-2 on Petroleum Products and Lubricants, on February 21. The meeting will be held from 2 to 5 P.M. at the Shoreham Hotel, Washington, D. C., in connection with the meeting of Committee D-2 of the American Society for Testing Materials. Visitors are welcome at the symposium.

American Society of Testing Materials. Shoreham Hotel, Washington, D. C., February 21. Symposium on Recent Developments in Instrumental Methods for Determination of Tetraethyllead in Gasoline

Fifth Annual Microchemical Symposium. American Museum of Natural History, New York, N. Y., February 24 and 25, 1950

Chemical Institute of Canada, Analytical Division. Royal Connaught Hotel, Hamilton, Ontario, March 2 and 3, 1950. Second annual symposium

Analytical and Microchemical Group. Philadelphia Section, AMERICAN CHEMICAL SOCIETY. Smith, Kline & French Laboratories, March 8

Symposium on Molecular Structure and Spectroscopy. Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio. June 12 to 17, 1950

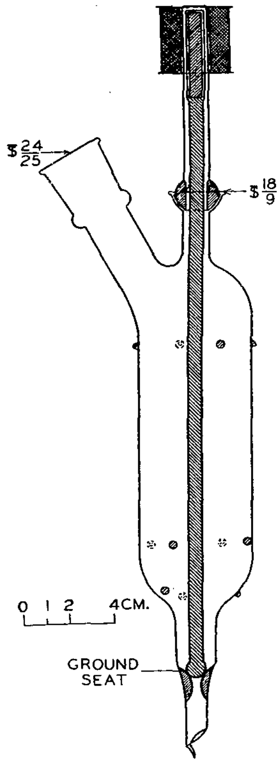
Third Annual Summer Symposium. Ohio State University, Columbus, Ohio, June 16 to 17, 1950

International Microchemical Congress. Graz, Austria, July 2 to 6

AIDS FOR THE ANALYST . . . . .

Improved Dropping Funnel. John Mitchell, Jr., and J. W. Henderson, Ammonia Department, E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.

In a previous publication from this laboratory [Lupton, J. M., Mitchell, J., Jr., Oemler, A. N., and Woolover, L. B., *J. Am. Oil Chem. Soc.*, **25**, 216–18 (1948)], a manually controlled dropping funnel (Dropolator) was described for use in the ashing of lard. More recently a similar dropping funnel was reported [Human, J. P. E., and Mills, J. A., ANAL. CHEM., **21**, 428 (1949)].



The Dropolator sample holder has been modified to permit better control in a wider number of applications. In addition to its use in delivering molten materials, the new unit can be employed for the controlled discharge of many solids. The transfer is essentially quantitative—for example, gravimetric checks during deliveries of 100-gram quantities of ethylene glycol and adipic acid indicated a holdup of less than 0.1 gram of sample.

The principal improvement involves the use of a timer-controlled feed rod instead of the manually operated drop control rod described in the earlier publication. In the new sample holder the rod (see figure) is enlarged at the lower end and ground to make a firm gravity seal with the ground seat. A magnetic iron plunger is sealed into the upper end of the rod. About a 2-mm. clearance is left between the top of the rod and the outer tube. The solenoid is controlled by an electronic combination on- and off-cycle repeat timer. (A suitable timer is manufactured by the C. C. Wilson Company, Chatham, N. J., and may be obtained from Eck & Krebs, 131 West 24th St., New York, N. Y.)

Positioning of the solenoid for optimum lifting of the control rod requires careful adjustment. This is done conveniently by clamping the solenoid to a rack and pinion mount. The spherical joint, held with a spring clamp, permits ready dismantling of the sample holder for cleaning purposes, etc., and the larger side-arm grind is more convenient for introducing solid materials. Both heating jacket and crucible holder are the same as those described previously, and the procedure is unchanged.

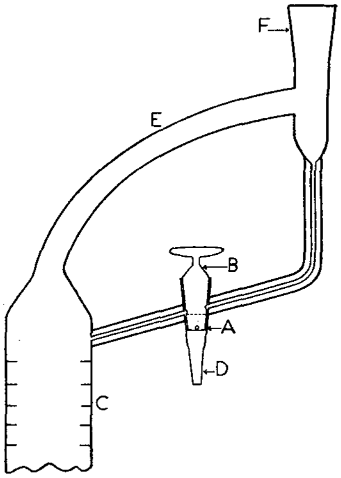
In addition to its use for lard, the versatility of this apparatus has been demonstrated by controlled deliveries of other liquids and several solids. Adipic acid was handled either as liquid or as solid. In the former case, the Nichrome ribbon–wound heating jacket was adjusted to maintain the adipic acid just above its melting point. In the latter, the dried solid, preferably in the particle size range of 20- to 60-mesh, was added at room temperature. There was no tendency toward caking when the solid was essentially dry. Comparative duplicate analyses of an adipic acid gave ash values of 13 ± 0.0 p.p.m. by the Dropolator method (delivered either as liquid or solid) and 16 ± 3 p.p.m. by the common dry-ashing procedure.

Other compounds which have been handled successfully include methanol, ethyl alcohol, nonyl alcohol, adiponitrile, isobutyl acetate, ethylene glycol, propylene glycol, linseed oil, and thiodipropionic acid as liquids; and thiodipropionic acid and sodium carbonate as solids.

Combination Sample Thief and Receiver for Operating under Reduced Pressure. J. Allen Brent, Jr., and J. Erskine Hawkins, University of Florida, Gainesville, Fla.

The removal of small samples of distillate for analysis when operating under reduced pressure is usually a somewhat tedious procedure. To simplify this operation a combination sample thief and receiver of simple design was constructed.

The main feature of this apparatus is a 14/35 standard-taper joint ground to fit a 1-mm. capillary tubing stopcock shell, *A*. Two holes about 0.5 mm. in diameter are drilled in the joint to align with the holes in the stopcock shell. The joint is then converted into the hollow plug, *B*, by sealing it at the bottom about 1 cm. below the holes and adding a handle. Another hole about 0.5 mm. in diameter is then drilled close to the bottom of the plug at an angle of 90° from the first holes. When the upper holes are aligned with the stopcock shell holes, the bottom hole is against the side of the shell. In this position liquid flows into the hollow plug and fills it to its capacity of approximately 0.3 ml. Additional liquid washes through and out the opposite side, where it flows into the graduated receiver, *C*. Because of its small capacity and the continuous replacement of distillate in the plug, the composition of the sample is that of the last few drops of distillate collected, for each volume indicated in the receiver.



To obtain a sample a small receiver equipped with a side arm and rubber bulb is connected to the 10/30 standard taper, *D*. *B* is turned through an angle of 90°, which aligns the bottom hole with a nick filed in the inside of the shell, which serves as an outlet to the receiver. After the sample is removed the plug is turned back to the through position. The bypass tube, *E*, of 14-mm. tubing ensures equal pressure in the receiver and the still head, to which this apparatus is connected with a 19/38 standard taper, *F*.

With this combination sample thief and receiver there is no necessity to break the vacuum, turn off the flow from the head, etc. This apparatus, although offering its greatest advantages when operating under reduced pressure, is equally satisfactory for use at atmospheric pressure.