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SYMPOSIUM ON SPECTROCHEMICAL METHODS OF ANALYSIS

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WALTER J. MURPHY, EDITOR

SYMPOSIUM

Spectrochemical Methods of Analysis

Introductory Remarks

DURING the past ten to fifteen years important strides have been made in the application of physical instruments to analytical problems of a chemical nature. The popularity of the various techniques which make up the science of instrumental analysis has increased from year to year and particularly during the present emergency have the many advantages of these analytical techniques become well known. Through their use a long list of analyses important to the accelerated production schedule of the industries of this country is being performed daily. Many of these analyses were formerly considered to be impossible; others, which are now completed automatically or within a few minutes at most, previously required up to several hours.

In developing and adapting these various instruments of physics to the problems and requirements of the chemist, the physicist and the instrument maker have rendered the subject of analysis an invaluable service. It has indeed been interesting to observe the various steps in the conversion of these research instruments of physics laboratories into commercially available devices for routine analysis and in certain cases into instruments for industrial control purposes. Although only a beginning has so far been made in the instrumentation of the subject of analysis, the successes already achieved are of such magnitude as to indicate much further work along these lines in the future. After the close of the war, much of the information now secret will undoubtedly be directly applicable to these problems, and many interesting instrumental developments may be expected.

The importance of instrumental analysis is attested by the number of pertinent publications which have appeared in recent years and by the frequency with which symposia on some phase of the subject have been sponsored by scientific societies. As the various methods reached higher and higher states of perfection, so also did the demands increase for more detailed information regarding the instruments, the techniques, the possible fields of application, and the potentialities of the methods.

In direct answer to such demands, the Division of Analytical and Micro Chemistry and the Division of Physical and Inorganic Chemistry held a joint symposium during the New York Meeting of the AMERICAN CHEMICAL SOCIETY on September 15, 1944. Since only one day could be devoted to this symposium, it was impossible to cover many of the instrumental developments which would have been interesting. The discussions were therefore limited to the general subject of Spectrochemical Methods of Analysis. The success of this symposium is a matter of record, and the officers of the two divisions and the speakers are to be congratulated.

Papers by Churchill (p. 66), Washburn, Wiley, Rock, and Berry (p. 74), and Mellon (p. 81) are printed in this issue; other papers will appear soon. It is hoped that their publication will prove interesting, helpful, and stimulating to many who were unable to attend the symposium.

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Analytical Applications of Emission Spectrometry

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The status of emission spectrometry as an analytical technique in the general analytical laboratory is discussed with particular attention to nonroutine applications. A number of techniques, involving qualitative and semiquantitative tests on a wide variety of materials, are described. Specific examples, drawn from the files of Aluminum Research Laboratories, are given to illustrate the usefulness of the spectrograph in general qualitative analysis in the identification of alloys, in seeking explanations for differences in physical and chemical properties, in the analysis of coatings and platings, in corrosion investigations, and in a variety of other special applications. The limitations, as well as the advantages, of spectrographic methods in qualitative and quantitative analysis are pointed out.

IN THE complete modern analytical laboratory, emission spectrometry occupies a place comparable in importance to gravimetric analysis or titrimetry. Used in combination with other analytical tools, the spectrograph often provides the analyst with information which might otherwise be unobtainable, and protects him both from failing to detect unexpected metallic elements and from making tedious, time-consuming, and sample-consuming tests for metallic elements which are absent or present in insignificant quantities. Occasionally, the laboratory encounters a problem which can be solved entirely by spectroscopic methods. More often the spectrograph is used as a preliminary to, or in combination with, other analytical techniques. The frequently encountered question, "Will the spectrograph eventually largely replace the chemist in metallurgical analysis?", is simply a manifestation of a popular misconception as to the nature and use of the spectrograph in the analytical scheme. With no more absurdity, one might inquire whether the analytical balance will eventually replace the analytical chemist. Both the spectrograph and the chemical balance are simply tools of the chemist's art, and either can be used effectively in simple, repetitive analytical procedures by routine operators who can lay no claim to being analytical chemists.

During recent years the most highly publicized phase of emission spectrometry has been its application to high-speed or large-volume routine quantitative analysis. The importance of this work is not exaggerated by the seemingly extravagant claims of those engaged in this work, or by the enthusiastic aggressive advertising of the instrument manufacturers. It is literally true that hundreds of thousands of dollars have been saved in applications, such as in the aluminum industry, in analytical costs alone, to say nothing of the benefits resulting from the speed of obtaining results. To the analytical chemist, however, routine quantitative analysis is of only casual interest, except in so far as he may be engaged in the supervision of such work, the development of routine methods, or the evaluation of the standard samples upon which the routine method is based.

The most important service of the spectrograph to the analytical chemist is the supplying of qualitative information with respect to the metallic and semimetallic elements. No other technique provides so much information with so little waste of time and effort. Qualitative analyses are almost completely objective, expected and unexpected elements being detected with the same ease and certainty. Moreover, smaller quantities of most elements are detectable by spectrography than by ordinary wet chemical tests. To be of any real value to the analytical chemist, a so-called qualitative procedure must actually yield semiquantitative information. The degree to which a spectrographic analysis is quantitative depends on the nature of the material analyzed, the conditions of excitation, the familiarity of the analyst with the particular element and matrix involved, and the extent to which standard samples are employed. In the roughest sort of qualitative analysis, the analyst is generally able to place the elements present in their proper orders of magnitude. Under very favorable circumstances, he may be able to make quantitative determinations of an accuracy comparable to or exceeding other methods of analysis. High quantitative accuracy is to be expected only in cases where the sample is compared directly or indirectly with very similar samples of known composition and when a method of excitation, peculiarly suited to the particular type of sample at hand, has been developed. In handling miscellaneous samples of a highly varied nature, it is not only impractical, but virtually impossible, to place a very large proportion of the spectrographic analyses in a general laboratory on a strictly quantitative basis because of the problems of standardization and excitation involved.

It is true that almost every analytical laboratory is called upon to perform the functions of a routine laboratory, at least occasionally. This circumstance may arise whenever the laboratory is required to analyze a large number of similar samples. In such cases, the laboratory may be able to develop a sufficiently economical quantitative spectrographic method to justify the time and expense involved in the preliminary experimentation, standardization, and calibration work required. Such procedures are routine in nature and are not within the scope of this paper. Of greater interest to the analytical chemist are the quantitative spectrographic analyses which can be used to good advantage in nonroutine work. There are four general cases where precise quantitative spectrographic analysis is feasible in nonroutine work: (1) when all other available methods of test are so difficult or time-consuming that the preliminary work involved in the spectrographic analysis is justified; (2) when no other method will give sufficient sensitivity of detection or sufficiently high accuracy; (3) when the sample available is too small to be analyzed by other methods; and (4) when a previously developed procedure and a suitable set of standard samples happen to be available when the sample is received. All four situations may occur rather frequently in the general analytical laboratory.

APPLICATIONS OF EMISSION SPECTROGRAPHY

From the point of view of the analytical chemist working with a diversity of materials in a nonroutine laboratory, the following qualitative or semiquantitative applications of emission spectrography are of greater interest and usefulness than the strictly quantitative applications.

PRELIMINARY TESTING OF UNKNOWNS. Probably the most important function of the spectrograph in the general analytical laboratory is the preliminary analysis of miscellaneous samples as a guide to quantitative analysis which is to follow. In most modern, general analytical laboratories every unknown sample is first examined spectrographically by a simple, more or less universal procedure which yields a dependable, sensitive test for the majority of the metallic elements and provides useful semiquantitative information. From the spectrographic data, the analyst not only learns what elements he should analyze for but is able to select the procedure, sample weight, and quantities of reagents most suitable for the amounts of the elements present. The analyst is protected not only from missing rare or unexpected elements but also from errors in analysis which might

have resulted from the interfering effects of these unexpected elements in his other quantitative determinations. Moreover, he is spared from having to run time-consuming chemical tests for elements that are not present in significant quantity.

IDENTIFICATION OF MATERIALS. The general analytical laboratory frequently receives samples on which the only datum requested is an answer to the simple question, "What is this material?" The material in question may be anything from a massive casting to a minute inclusion detected microscopically in a piece of metal. It may be a thin plating, a sample of rock, a patent medicine, or mysterious precipitate. Such problems are often solved completely by a spectrographic test. In other cases a spectrographic test may be used in combination with chemical tests for acid radicals, organic compounds, or other constituents which the spectrograph will not detect. Some of the analytical jobs falling in this general category may require an approximate quantitative analysis, as, for example, in the identification of an alloy, or the determination of the grade of some standard product for which a grading system based on purity has been established.

COMPARISONS BETWEEN SIMILAR MATERIALS SHOWING DIFFERENCES IN PHYSICAL OR CHEMICAL BEHAVIOR. Another very important category of problems in which the spectrograph is highly useful is in the comparison of materials of similar type but manifesting different properties. Metallurgical laboratories frequently receive samples of alloys having unusually good or unusually poor mechanical properties or resistance to corrosion. In such cases a simple spectrographic comparison between normal and abnormal materials often yields important information, in some cases not only solving the problem at hand but occasionally providing information which may lead to improvements in the product. Similar applications are frequently encountered in comparing satisfactory and unsatisfactory reagent chemicals, catalysts, paint coatings, and a host of other materials.

CHECKING CHEMICAL SEPARATIONS. In the development and improvement of wet chemical methods and in checking the validity of certain existing methods, emission spectrography provides an excellent means of studying the completeness of separations, the purity of precipitates, and the nature of any fractions such as insoluble residues, or precipitates of unknown composition which may occur in experimental analytical work.

MISCELLANEOUS QUALITATIVE AND SEMIQUANTITATIVE STUDIES. In investigational work, numerous special applications of the spectrograph, not included in the foregoing categories, are encountered. For example, the spectrograph has been very valuable in corrosion studies, both in diagnostic analyses of the corroded metal and corroding medium and in tests designed to determine the likelihood of corrosion by testing both the metal surface and its environment. Another valuable type of application is in making qualitative or semiquantitative surveys involved in studying the occurrence and distribution of the rarer elements, in tracing the origin of minor impurities in products whose manufacture involves the use of a large variety of raw materials, in following the progress of purification processes, and in making large-scale statistical studies. In many of these applications, the spectrograph provides the only feasible means of obtaining the desired information. The economy and speed of the spectrographic method often enable the analyst to obtain a much greater volume of data, thereby making the final results more conclusive.

APPARATUS

The minimum basic spectrographic equipment of a general analytical laboratory includes a spectrograph, a darkroom, a simple excitation source, such as the direct current arc, and a few sundries and accessories necessary for the development of films or plates, the preparation of samples, and the viewing of spectrograms. With this minimum equipment, the analyst can do much of the qualitative and semiquantitative spectrographic work discussed. To obtain the maximum usefulness out of the spectrograph, considerably more elaborate equipment is required and the additional cost is almost always amply justified. Today, the general analytical laboratory cannot be considered complete without the following:

A flexible, relatively high dispersion spectrograph, either one of the larger grating instruments or one of the so-called "automatic" quartz prism instruments.

A direct current arc source.

A conventional spark source or, better, one of the newer, highly flexible excitation units which will produce the equivalent of any of the conventional sources.

Equipment for accurately controlling the development and processing of films and plates.

A comparator or projector suitable for the visual examination of spectrograms, preferably equipped with a wave-length scale and with some provision for comparing two or more plates or films.

A reliable densitometer, also preferably equipped with wave-length scale and a provision for comparison with a reference spectrogram. The comparator and densitometer may be combined in one instrument.

Chemical and mechanical facilities for the preparation of samples.

A large variety of accessories, including arc stands, spark stands, electrode holders, tongs, forceps, electrical and optical testing equipment, timers, etc.

Wave-length tables, spectrum atlases, and reference books.

The specific makes of instruments and the design of the various accessories desirable in a particular laboratory depend on the scope and nature of the analytical work anticipated. More specific recommendations along these lines can best be obtained from laboratories that have had spectrographic experience in applications of similar character.

GENERAL TECHNIQUES

USE OF THE DIRECT CURRENT ARC. Despite the emphasis on various types of controlled sparks and on elaborate new sources recently placed on the market, the direct current arc remains the most widely used and most generally applicable excitation source in nonroutine applications. While the controlled spark is much more widely used in routine quantitative work and performs functions for which the direct current arc is inadequate, the direct current arc is more nearly indispensable than the spark in general qualitative and semiquantitative analysis. The arc owes its general superiority in such applications to the high sensitivity of detection it provides and to the fact that it can be used conveniently on almost any type of sample.

All direct current arc techniques are very similar and the differences that exist are generally superficial modifications necessary to increase the stability of the arc in a particular application or to favor the detection of elements of special interest in a particular test.

In virtually all cases a small portion of the sample (usually not over 10 mg.) is volatilized in an arc operating at from 4 to 15 amperes. The light from the entire arc or from the central portion of the arc is ordinarily used for the analysis. (Special techniques, such as the cathode layer, will not be considered here.) If the submitted sample is of suitable dimensions and properties, one or both of the electrodes may be specimens formed from the sample. In this case, the arc is operated for a timed interval determined by previous experience. More often, a small portion of the sample is placed in a crater formed in the end of a graphite electrode. This electrode is used as the lower electrode in the arc and is usually positive. Another graphite rod is used for the negative upper electrode. An arc of this type is more generally applicable to the variety of samples received in a general laboratory and is usually more satisfactory than an arc using self-electrodes because it enables the operator to volatilize completely a known amount of sample and because it affords greater sensitivity in the detection of small amounts of the elements less easily excited in the arc.

The arc is essentially a thermal phenomenon. The elements present in the sample must be vaporized before they are excited and the more volatile elements will be volatilized and excited first. The temperature attained by the electrodes is controlled

by the amperage applied, the relative amounts and boiling points of the elements present, and the conditions surrounding the arc which affect the transfer of heat. When the sample placed in the electrode crater contains constituents of widely different boiling points, the elements of highest boiling point volatilize relatively slowly, if at all, in the early stages of the exposure and do not attain maximum excitation until the more volatile substances have been vaporized. When self-electrodes are used, minor elements of lower volatility than the matrix are often very difficult to excite, and sensitivity of detection is correspondingly low. For example, molybdenum is not detected in aluminum alloys containing up to a few hundredths per cent when self-electrodes are used, but can be detected in amounts less than 0.001% when a small sample of the alloy is completely volatilized in a graphite arc.

The successive excitation of the elements in the inverse order of volatilities makes possible an increase in sensitivity of detection for any given element by photographing only that portion of the arcing cycle during which the intensity produced by that element is at a maximum. To do this by means of a single exposure requires that previous data be available which will enable the analyst to select the proper portion of the arcing period for the test. A more practical scheme, when extreme sensitivities are required, has been used occasionally in some laboratories. This system is generally referred to as the moving plate technique and consists of simply moving the photographic plate vertically, either at frequent regular intervals or in a slow continuous motion during the arcing cycle. While this technique is useful in particular cases, it is not generally necessary or particularly desirable in most spectrographic analysis because of complications and uncertainties introduced in attempting to integrate intensity over a period of time in making quantitative estimates and because simpler, less elaborate techniques are generally adequate.

Graphite is almost universally used for arc electrodes in general qualitative and semiquantitative work. Unlike metallic electrodes, it will not melt or form a crust of oxide. Moreover, it is easily formed to the desired shape and, most important of all, it is obtainable in the extremely high purity necessary for many purposes. Graphite electrodes could not, of course, be used in testing for carbon. However, carbon tests are rarely made spectrographically and are considered impractical in many spectrographic laboratories.

For certain purposes, the so-called "regular" grade spectroscopic graphite is useful and electrodes of this grade are obtainable from at least four manufacturers in the United States. These electrodes are very inexpensive (approximately 6 cents per foot for 0.25-inch diameter rods) and may be purified by chemical treatment or by high-temperature exposure to various atmospheres to increase their applicability to the analytical problems of the general laboratory. However, laboratory methods of purification are not completely satisfactory and even the purified electrodes are unsuitable for general qualitative work when minor impurities are important. A very high-grade graphite, sold under the designation "special spectroscopic graphite", is the only graphite available in sufficient purity to be generally applicable in qualitative analyses for minor constituents. As far as is known to the author, graphite of this grade is obtainable from only one manufacturer and the cost is understandably much higher than the "regular" or intermediate grades available elsewhere.

In Aluminum Research Laboratories and in many other laboratories having a similar diversity of problems, it has been found expedient to standardize on the special spectroscopic graphite rods, not only because a large proportion of the analyses made actually require graphite of the highest purity but also because of the risk of mixing the grades in a busy laboratory in which a large number of analysts are doing similar work. There are, of course, occasional instances where other supporting electrodes are used. Since the special spectroscopic graphite has been available, the use of supporting electrodes other than graphite has been largely restricted to tests for carbon, tests in which the cyanogen bands produced in the graphite arc are objectionable, and specific tests in which less expensive electrodes, such as copper, can be used. Some spectrographers prefer ungraphitized carbon rods to graphite rods. The extensive use of ungraphitized carbons has been prevented by the difficulty in shaping electrodes from this material.

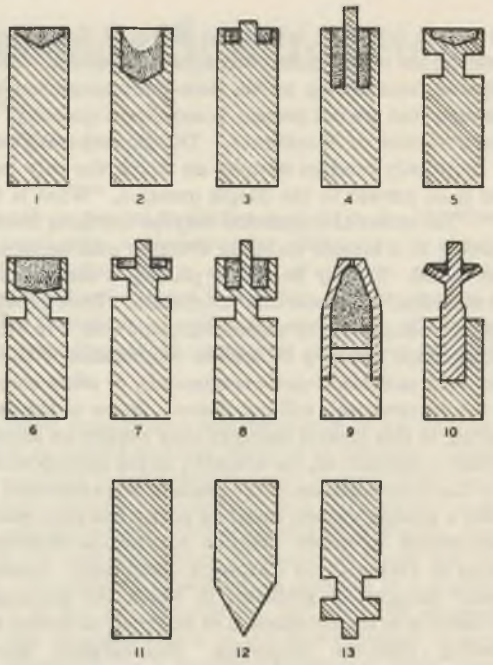

Figure 1. Typical Graphite Electrodes Used with the Direct Current Arc
1 to 10, lower electrodes
11 to 13, upper electrodes

There are almost as many different shapes of supporting electrodes as there are laboratories doing arc work. Most of these differences are simply minor variations in dimensions and are not particularly important. Figure 1 shows a typical assortment of electrodes representing the most generally used types.

No. 1 is a simple shallow cup drilled in the end of a 0.25-inch electrode. This is probably the most widely used type for miscellaneous qualitative and semiquantitative analysis. No. 2 has a deeper cavity and is widely used when the sample is introduced into the cavity as a solution or suspension. In such cases the electrode is dried before arcing. Nos. 3 and 4 are modifications of Nos. 1 and 2, respectively. The addition of the center post reduces the wandering of the arc. Nos. 5, 6, 7, and 8 are the so-called necked electrodes. Necking the electrodes aids in attaining higher electrode temperatures by reducing the withdrawal of heat by conduction along the electrode. Nos. 9 and 10 are special purpose electrodes, developed by and sold in fabricated form by Applied Research Laboratories. No. 9, the boiler electrode, is potentially useful in specific tests for the more volatile elements and in the moving plate technique. This electrode is specifically designed to enhance preferential distillation effects in the arc. No. 10, known as the platform electrode, has been used in the quantitative analysis of refractories, ore materials, and steel samples.

Nos. 11 and 12 are the most generally used upper electrodes, No. 11 being simply a short length broken or sawed from a graphite rode, and No. 12 having been sharpened in a pencil sharpener or other cutting device. No. 13 is an upper electrode developed for use with the platform electrode, and necked to aid in attaining high arc temperatures. When used with samples containing large amounts of alkali, this form of upper electrode is effective in preventing the crawling of the arc up the sides of the upper electrode.

The majority of laboratories use 0.25-inch rod in the preparation of electrodes, but some use 0.125-, $^3/_{16}$-, and $^5/_{16}$-inch rods. There is also a rather wide range of cavity depths, center post heights, and wall thicknesses in use in various laboratories. While the thirteen electrodes shown illustrate the most important distinct types, special shapes are often devised for handling individual samples or for certain specific tests. In testing for small amounts

of mercury, arsenic, or other volatile constituents, a very deep cavity (sometimes 0.5 inch or more) of small diameter has been found effective. Such an electrode permits the distillation of the volatile elements from a relatively large sample.

The center post and the pointed upper electrode are both effective in reducing the amount of wandering of the arc during exposure. It is particularly desirable to keep the arc well centered with respect to the electrodes when the arc image is focused directly on the slit of the spectrograph. It is much less important when an image is focused on the grating or collimator of the spectrograph. In this case a magnification can be selected at which the arc image will remain within the collimator or grating as the arc wanders around the periphery of the electrode tip and the use of center posts and pointed upper electrodes becomes unnecessary. A center post makes an electrode somewhat less convenient in loading and slightly enhances the band spectra produced by the carbon compounds formed in the arc.

Simply placing a portion of the sample in an electrode crater and applying current will not usually produce an arc suitable for general analytical purposes. Most metal samples will spit and sputter and, in some cases, accumulations of oxide will form and interfere with the stability of the arc. Hydrated salts or oxides will evolve water vapor so rapidly that they will be largely expelled from the arc before a representative spectrum has been obtained. A similar performance is to be expected for any sample containing highly volatile salts or compounds that decompose with the evolution of gases or react with violence under the influence of the sudden rise in temperature when the arc is struck. Samples containing compounds of low volatility or containing elements which form such compounds in the arc often form small molten beads which frequently roll out of the cavity during arcing.

Most of the above effects can be largely eliminated by the proper preparation of the samples for arcing and by the admixture of certain substances with the samples. The first and most obvious step in this direction is the preliminary heating of the sample to eliminate water and to decompose any unstable compounds tending to cause sputtering or loss of sample in the arc. Sometimes a chemical treatment is necessary to convert the original compounds present into compounds more amenable to arcing. In many cases it is further desirable that the sample be diluted with some noninterfering material which will prevent the formation of mobile beads of molten salt, oxides, or metals, and will assist in the volatilization of elements of high boiling points or elements existing in extremely nonvolatile compounds.

Chemical analysts in the field are sharply divided as to the type of material most suitable in accomplishing these ends. One group prefers the addition of a volatile or highly reactive material which will mechanically spray the sample up into the arc. Ammonia salts are the most common additions of this type and many analysts add ammonia salts in all general qualitative and semiquantitative work. While this method represents an improvement over the simple arc in which no diluent is used, it does not provide the best sensitivity and dependability in dealing with such materials as alumina, zirconia, or columbia. The other group of analysts, of which the author is a member, advocates doing all possible to prevent loss of sample by spitting or spraying and accomplishing the excitation of elements forming refractory oxides by chemical reduction.

Both ends are accomplished by the addition of powdered graphite. For best results the sample is finely ground and very intimately mixed with at least twice its weight of graphite. Such a mixture yields a steady arc with a minimum of spraying. The most refractory oxides are decomposed and the sample is volatilized in a relatively short exposure. The molten salts or oxides are largely prevented from forming beads. Rather high reproducibility of excitation is achieved and the sensitivity in detecting such elements as zirconium, molybdenum, and columbium is much improved over the mechanical spraying method. In most cases the spectrum of carbon and carbon compounds is actually weaker than when no graphite is added, since the exposure time required for complete volatilization is much reduced. Metallic samples may be handled in a similar way, the finely divided particles required being generally obtained by filing.

In many cases it is desirable or necessary to introduce the sample into the electrode as a solution. This situation arises frequently when the material to be analyzed is too small to be conveniently handled as a solid and in comparative analyses where the amount of the sample introduced into the electrodes can be controlled most conveniently by measurement of volume. The use of solutions often provides a convenient means of adding an internal standard when quantitative or semiquantitative data are sought and facilitates the preparation of synthetic standards.

In some cases the solution is simply introduced into the electrode cavity and dried by heating; in this case a large part of the sample will be absorbed by the electrode. Some spectrographers arc the electrodes prior to introducing the sample, for the double purpose of purification and promoting the absorption of the sample. Other spectrographers prefer to treat the electrode cavity with some noninterfering material which will prevent absorption. Either an acetone solution of cellulose acetate or kerosene is satisfactory for most cases. Sealed electrodes, in general, will yield higher sensitivities of detection, better reproducibility, and spectra which are weaker in band structure from carbon compounds. When substantial quantities of aluminum, zirconium, titanium, or other elements forming oxides of relatively high boiling points are present, the performance of the arc is improved by introducing powdered graphite or carbon into the cavity before adding the sample. The graphite powder promotes the volatilization of such elements and reduces the tendency towards forming molten beads of oxides.

In most laboratories, samples are introduced into the electrodes as solutions only in special cases. When a sufficiency of sample is available, better results are generally obtained by evaporating the solutions to dryness, igniting to remove water and to decompose the less stable salts, intimately mixing the residue with graphite or carbon, and introducing the mixture into the electrode as a solid.

Alternating Current Spark. Spark excitation may be of use to the general analytical laboratory in the following cases:

When the results obtained on the direct current arc are not sufficiently quantitative.
When a metal specimen is to be analyzed with a minimum of danger to the specimen.
When the test is to be restricted to a metal surface or to a particular small region of a metal sample.

Most analyses can be made somewhat more precisely from a quantitative standpoint by using a condensed spark discharge.

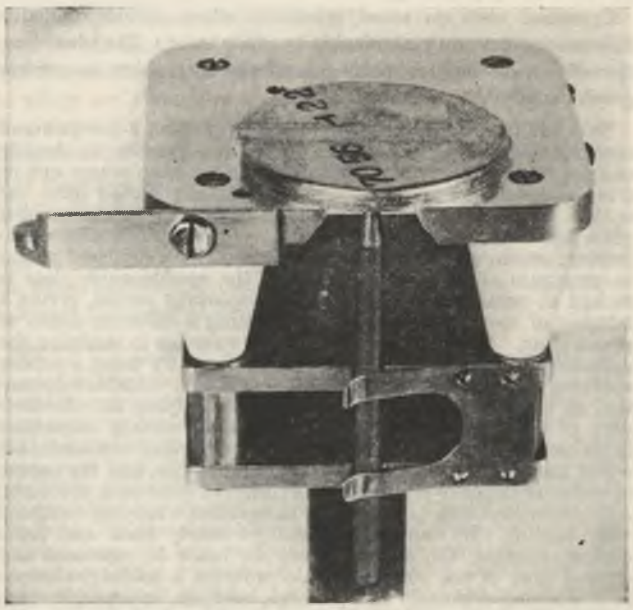

Figure 2. Petrey Spark Stand

Semiquantitative analysis of a somewhat higher grade than that provided by the arc is often required in the general laboratory in the identification of alloys and in seeking small differences in composition between various types of samples. In the case of metallic samples, both spark electrodes may be cut from the sample and sparked directly. Cases are frequently encountered where the size or shape of the submitted sample is such that only one electrode can be prepared conveniently from the sample itself. In such cases an alter electrode of graphite is used. In Aluminum Research Laboratories and in many other general laboratories, it is general practice to use the sample as one electrode (usually the upper) and a graphite rod as the other electrode. The Petrey stand (Figure 2), which is now widely used in quantitative spectrographic analysis, was originally developed for general spark work and is so used in a number of laboratories. Any sample having a surface large enough to cover the aperture in the top plate can be sparked by simply laying it on the spark stand. Various clamps and adapters are used to hold very small samples in place.

While spark spectra have been used less frequently for increasing quantitative accuracy on nonmetallic samples, the spark can be applied very effectively to salts, oxides, rocks, and miscellaneous powders. The sample is mixed with de-ashed natural graphite (1 part sample, 2 parts graphite) and pressed into a pellet which is used as one electrode in the spark. This method yields results almost equaling those obtained in sparking metal samples in some cases. Quantitative analyses of materials for which no chemically analyzed standards are available can be carried out with synthetics by the pressed pellet technique, providing synthetics having similar composition and states of combination of components can be prepared. For example, a metal sample can be converted to oxides by chemical treatment and compared with samples of oxides prepared from volumetric solutions of metal salts.

Many laboratories are frequently asked to analyze metal specimens whose intrinsic or historical value or whose practical utility makes it necessary to analyze the specimen with as little damage as possible. Often spark excitation is the best means of obtaining the information desired with a minimum of damage to the specimen. In cases of this kind, a low-powered spark is played on a selected area of the sample from a graphite electrode. The spectrum so obtained is compared with spectra prepared in the same way from samples of known composition. When the tests are complete, the last evidence of the sparking can usually be removed by polishing.

Localized tests on metal specimens often provide valuable information not easily obtainable by other tests. The identification of thin coatings and platings is a frequent problem in spectrographic analysis.

Such identifications are easily made by playing a low-powered spark discharge on the surface. Often it is possible to identify each of several layers of a coating, as in the case where one or more different metals have been successively plated onto the surface. In such cases, a technique analogous to the moving plate technique is sometimes useful. The spark is allowed to impinge on the given spot on the specimen for a sufficient period to penetrate all of the coatings, and the spectrograph plate is racked at regular intervals during the sparking period, giving a number of spectrograms each representing a different depth of penetration. Such tests are sometimes valuable in studying the diffusion of the base metal into the coating. By using a similar sparking technique, it is often possible to obtain valuable information on metal surfaces which may aid in studying the effectiveness of cleaning methods, the presence of surface impurities introduced in fabrication, the presence of surface contaminants which may have a bearing on corrosion problems, and the nature of stains or deposits of unknown origin. In some such problems, Aluminum Research Laboratories have found a moving electrode very helpful. By moving the sample slowly back and forth during sparking, the exposure may be made to represent any desired area of the surface. This provides a useful technique in identifying extremely thin platings, coatings, or deposits which are quickly penetrated by the spark, and in obtaining information as to average surface composition over a selected area.

Other Excitation Sources. Many analytical laboratories make extensive use of excitation sources other than the simple direct current arc and the condensed spark. Most important of these from a standpoint of current usage is the alternating current arc. While this source is not an essential piece of equipment in most laboratories, it has been very useful in specific applications. In general, the sensitivity of detection, stability, and field of application are intermediate between those of the direct current arc and the condensed spark. Without any intention of derogation, the alternating current arc is omitted from this discussion because the techniques used, the results obtained, and the scope of application are largely included in the general remarks pertaining to the other two sources. In most applications, the alternating current arc is a good compromise between the alternating current spark and the direct current arc, and as such it will serve a few purposes better than either of the other two sources.

Looking to the future, the most important excitation sources, other than the direct current arc or the alternating current spark, are the highly flexible, all-purpose units such as the Multisource. While "Multisource" is the trade name of a particular excitation unit, it represents a type which may become popular in the future. The Multisource is highly flexible and is equipped with all the most effective devices for regulation and control of the discharge. It is capable of producing discharges equivalent in most respects to the direct current arc, the condensed spark, and the alternating current arc, as well as a number of intermediate discharges not available on other units. This unit can be used in place of other excitation sources in many applications, and the Multisource or equivalent apparatus may eventually replace the source units now more or less standard equipment in many spectrographic laboratories.

Laboratory Report

Aluminum Company of America

Aluminum Research Laboratories
Analytical Division
New Kensington, Pa.

No. 00000

June 1, 19 44

Sample Of: Miscellaneous Materials

Received From: John Doe

Date Received: June 1, 1944 Marked

Description

Qualitative Spectrographic Analysis

	Clay	Ash of Decorator's Tape	Ash of Plum Pudding (Canned)
Major Constituents:	Silicon Aluminum	Zinc Calcium	Sodium Potassium
1 to 10%:	Iron Calcium Titanium	Silicon Aluminum Phosphorus Sodium Boron	Calcium Aluminum Phosphorus Magnesium Silicon
0.1 to 1.0%:	Sodium Potassium Magnesium	Iron Magnesium Copper Barium Manganese	Iron Boron Strontium
.01 to 0.1%:	Strontium Barium Vanadium Manganese Zirconium	Fluorine Tin Antimony Titanium Lead Chromium Strontium Nickel	Manganese Copper Tin Lithium
Less than .01%:	Lithium Chromium Nickel Gallium Molybdenum Germanium Copper Zinc Lead Tin Silver	Lithium Molybdenum Silver Gallium Cadmium	Lead Barium Gallium Zinc Chromium Nickel Silver

Original To John Doe
Copies To

Analyzed By A.B.C. Date June 1, 1944 Approved By Chief Chemist

Figure 3. Typical Report of Qualitative Spectrographic Analyses

SPECIFIC APPLICATIONS

The remainder of this discussion is devoted to practical examples illustrating the usefulness of emission spectroscopy to the analytical chemist. All this material is based on work performed at Aluminum Research Laboratories.

Figure 4. Spark Spectra of Five Typical Aluminum Alloys

General Qualitative Analysis. All miscellaneous samples submitted for complete chemical analysis are first tested qualitatively as follows:

A portion of the sample is prepared for arcing. On nonmetallic samples this usually involves ignition to remove water, grinding to a fineness approximating 200-mesh, and mixing with graphite (2 parts graphite to 1 part sample). In special cases where small amounts of mercury, arsenic, or other volatile elements are likely to be present, a separate sample is prepared without ignition, and both ignited and unignited samples are analyzed. In the case of metal samples, the preparation usually consists of preparing a small amount of fine filings from the sample and mixing with graphite. In some cases graphite may be omitted if the metal is one which is easily volatilized without spitting. In this case a small fragment of the metal may be used instead of filings. In other cases the metal may be converted to salts or oxides by chemical treatment, and the salts or oxides prepared for arcing as described for nonmetallic samples.

A portion of the sample is placed in the crater of an electrode of the type designated as No. 1 in Figure 1. This electrode is used as the lower electrode in the arc and is positive. An arc current of 12 to 15 amperes is used on all samples which are mixed with graphite. On metal particles analyzed without graphite, the arc current is usually reduced to 4 or 5 amperes, at least for the initial stages of arcing. In all cases, except in specific tests for the more volatile elements, the arcing is continued until the sample is completely volatilized.

The spectrum is recorded on an Eastman Type 103-L or Type I-L plate. The test is repeated at two or more different settings of the spectrograph to cover a range of wave lengths including sensitive lines of all of the elements sought. On a Gaertner two-lens spectrograph, two exposures are required, one extending from 2275 to 4000 Å., and the other from 2800 to 8500 Å. If the sample available is sufficient for only one exposure, the region 2490 to 6000 is used. On other spectrographs the wave-length ranges will be different and three exposures may be necessary to include a sufficient wave-length range. An iron arc spectrum and occasionally one or more additional reference spectra are photographed in juxtaposition with each spectrum or group of spectra in each region. The plate is developed and processed by conventional methods.

For interpretation, the spectrogram is viewed on a viewing box or, more often, projected on a screen at a magnification of about 10 to 1. The analyst identifies the lines of the various constituents present by the positions of the lines relative to the iron spectrum. Quantities are estimated by relative blacknesses of line images and the estimation is largely based on the previous experience of the analyst and comparisons with spectra of samples of known composition.

Three typical qualitative analyses reported on the form used by Aluminum Research Laboratories are shown in Figure 3. The percentage groupings are based on the visual estimates of the analyst and are intended to give the approximate percentage of any one element with respect to the total amount of all elements detected. While this same type of report is used on all general qualitative analyses, the report must frequently contain additional data, such as loss on ignition, total solids, or other information which may be required for interpreting the report.

The interpretation of qualitative spectrograms is the most difficult job in the spectrographic laboratory. The quality of the results is directly proportional to the experience and judgment of the analyst. He must be thoroughly acquainted with the principal lines of all of the elements and must know which lines are interfered with by lines of other elements, and to what degree. He must be thoroughly familiar with the iron spectrum and must have a tremendous accumulated memorabilia of data which will enable him to exercise dependable judgment in the estimation of quantities. He should have a broad knowledge of the typical compositions of the myriad different materials he may be called upon to analyze and must be acquainted with the effects of different matrices and different techniques of excitation on the spectral response obtained from the elements.

Alloy Identification. Often a familiar alloy can be identified by a simple qualitative analysis made by the technique in the foregoing paragraphs. Of course, in most cases a complete qualitative examination is not required, since minor impurities are usually of little importance in determining an alloy. However, it is often necessary to make an analysis of greater quantitative accuracy than the usual qualitative examination in order to distinguish between alloys of similar composition. General practice in this laboratory is to make a simple qualitative examination by means of arc spectra to determine the general type of alloy, and to follow this with a spark test in comparison with appropriate samples of known composition. Figure 4 shows the spark spectra of a number of aluminum alloys. These spectra were prepared by using a machined or filed surface of the sample as the upper electrode on the Petrey stand and a hemispherically tipped graphite rod as the lower electrode.

It has been claimed in several metallurgical laboratories that the determination of alloys by the spectrograph would be ample justification for the cost of the equipment, if there were no other use for the apparatus.

A case in point occurred in a plant where a large number of aluminum tubes had been cut very accurately to specific lengths and given a special polishing treatment. In a batch of several thousand tubes it was suspected that a few of the tubes were of the wrong alloy. Since the tubes had already been cut and carefully finished, the removal of analytical samples would have meant the rejection of all tubes sampled. The problem was solved by taking all the tubes to the laboratory and identifying the alloys by spectra prepared by playing a weak spark discharge on the surfaces. The tubes of the incorrect alloy were easily sorted out and the slight blemish left by the spark was removed by polishing the remaining tubes.

Very frequently an alloy identification is required on a sample which is too small for positive identification by other means. This frequently occurs in the case of aluminum alloys, where the alloys are often very complex. The chemical identification of an aluminum alloy may require tests for eleven different constituents and even after testing for the eleven common additions, there is the risk of missing some unusual constituent, especially on very small samples.

Comparisons between Materials Showing Different Properties. A typical example of a simple analytical comparison, which had far-reaching consequences, occurred in Aluminum Research Laboratories several years ago.

One of the workers in the metallurgical laboratory was instructed to prepare several batches of an aluminum alloy and was given the compositions to be used in synthesis. The series was to contain various amounts of copper and manganese, and the usual impurities present in the range of 25S alloy. In subsequent tests, one of the alloys produced was found to have exceptionally high properties for this alloy and was inconsistent with the other members of the series. A chemical analysis had been made for the elements added and all the impurities to be expected from the raw materials used. No explanation for the unusual properties was obtained and the matter was largely forgotten until a year or so later when a spectrograph was installed in the laboratories. One of the metallurgists still had a specimen of the metal showing the unusual properties and submitted

the sample for spectrographic examination. A simple arc spectrum comparison between this sample and a sample of a similar alloy showing normal properties revealed that the abnormal sample contained a few hundredths of a per cent tin. The effect of tin was soon verified by intentional additions, and a new alloy was born.

Such comparisons among metal specimens and among other types of samples are frequent occurrences in this laboratory, although they are not always of as great ultimate importance.

Another typical problem involving a semiquantitative comparison between samples showing different properties arose in connection with corrosion studies made at Aluminum Research Laboratories.

For many years corrosion investigators had used water from a certain municipal supply as a standard test medium because of its unusual pitting action on aluminum. To improve the reproducibility of test conditions over long periods and to avoid the inconvenience involved in collecting and shipping the water, it was decided to duplicate the municipal water by chemical synthesis. Chemical analyses of this water over a period of years were available and from these data the average composition was calculated and a test water was prepared by adding appropriate amounts of the various salts to distilled water. Unfortunately, this test water did not duplicate the behavior of the municipal water and was, therefore, altogether unsuitable.

Samples of the municipal water and of the synthetic product were submitted to the analytical laboratory to determine the difference in composition. Portions of each were evaporated to dryness and the residues were compared spectrographically by means of arc spectra. The spectrograph revealed that the city water contained small amounts of a number of heavy metals not present in the synthesized water. Further chemical and spectrographic tests were made to determine the quantities of these minor constituents, and a second synthetic sample was prepared containing appropriate additions of salts of these minor constituents. This water was found to be equivalent to the original city water and has since been used as a standard corrosion test medium.

Both of the foregoing illustrations were taken from the records of several years ago when the spectrograph was just beginning to come into its own. While they are cited as typical examples of spectrographic applications, the order of events is usually somewhat different today. When an experimental alloy is prepared or when a material is to be duplicated by synthesis, a spectrographic analysis is generally made at the outset and not as an afterthought. Nevertheless, one of the most useful activities of the spectrographer is in the detection of differences in composition which may explain why two or more apparently similar materials differ in chemical or physical properties, and the spectrograph has provided useful information in thousands of such problems in Aluminum Research Laboratories.

Corrosion Investigations. Owing to its high resistance to corrosion in most environments, aluminum is often employed in applications where corrosion of metal parts is the chief hazard. When failures occur, the spectrograph often provides a means of determining the cause of corrosion, thereby providing information necessary in preventing future failures. The spectrograph is particularly useful when the corrosion has been caused by the presence of heavy metals, such as copper or tin, in contact with the aluminum or of salts in solutions which are in contact with the aluminum. When the corrosion has been caused by excessive alkalinity or acidity, the spectrograph is generally less useful, although in the former case it may provide valuable information concerning the presence or absence of specific alkali elements.

The plan of attack on a corrosion problem presented to the laboratory may vary widely, depending on the nature of the samples submitted and the analyst's knowledge of the history of the samples. For purposes of illustration, let it be assumed that the analyst has insufficient historical information concerning the corroded metal to form a definite opinion as to the nature of the attack and that he is able to obtain the necessary samples for test purposes. Under these circumstances, a complete series of diagnostic tests would include the following:

1. Spectrographic analysis by means of arc spectra of any corrosion products removable mechanically.
2. Localized tests in the corroded areas by the use of arc spectra of nitric acid leaches or spark spectra obtained by sparking selected areas.
3. Semiquantitative comparison of 1 and 2 with uncorroded portions of the specimen to determine which of the elements detected in the corrosion products or on the corroded surface may have originated in the metal itself and which are contaminants.

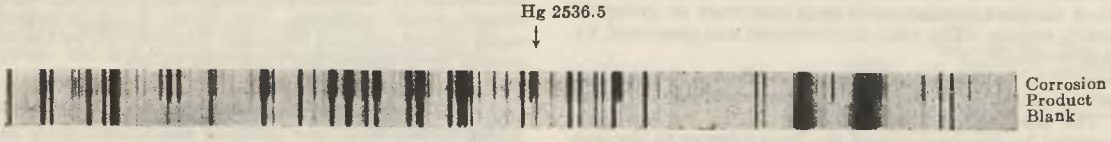

Figure 5. Arc Spectra of Corrosion Product and Blank from Aluminum Pitcher

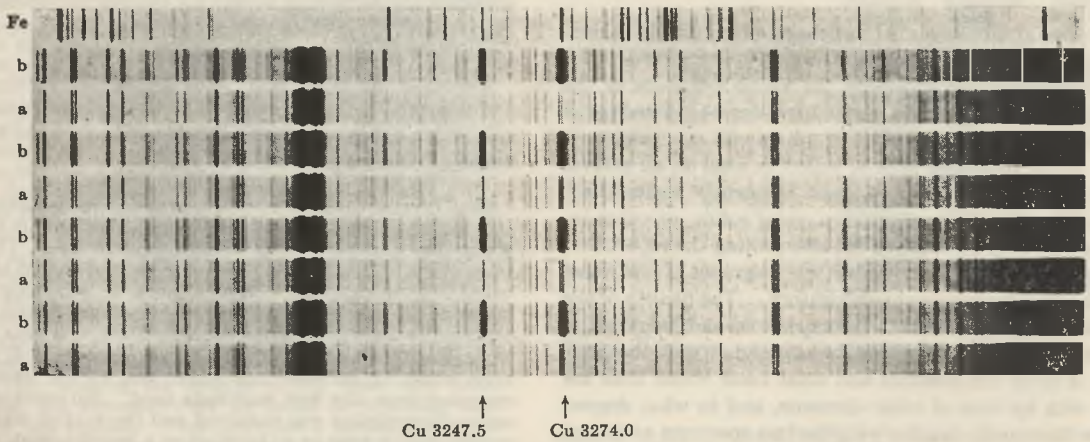

Figure 6. Spark Spectra of Surfaces of Spot-Welded Magnesium Sheet

a. Unblackened areas of sheet
b. Blackened areas of sheet

4. Qualitative spectrographic analysis of a carefully cleaned portion of the metal itself.
5. Qualitative examination of any metal parts, solutions, or other materials which had been in contact with the corroded metal when the corrosion occurred.
6. Supplementary chemical tests including tests for acid radicals, pH determinations on the corrosion product and on any materials making up the environment of the corroded specimen.

Obviously, in specific instances some of the foregoing tests may not be required. Frequently, the spectrographic examination, together with the investigator's knowledge of the case, may provide the complete solution. In other cases the spectrograph may provide only negative information, enabling the investigator to eliminate certain possibilities. Following are two examples of corrosion problems which were solved by simple spectrographic tests:

An aluminum pitcher had failed in service in a hospital. Since aluminum pitchers ordinarily gave excellent service in such applications, the pitcher was sent to Aluminum Research Laboratories to determine the cause of corrosion. As received in the laboratory, the pitcher showed a number of perforations through its bottom, but all visible traces of corrosion product had been removed by washing and scouring at the hospital. The perforated areas were leached briefly in hot concentrated nitric acid. An uncorroded piece of the metal was carefully cleaned to remove all surface contaminants and leached as a blank determination. The two leaches were evaporated to dryness in a water bath and the residues mixed with graphite powder and compared spectrographically by volatilization in a direct current arc. Examination of the spectrograms revealed that mercury was present in appreciable quantity in the corroded area, thus providing a convincing explanation for the corrosion. In Figure 5 is shown an enlargement of the portion of the spectrograms which includes the sensitive mercury line at 2536.5 Å. It was thought probable that a thermometer had been broken in the pitcher, thus introducing the mercury and initiating the corrosion.

A piece of equipment made from spot-welded magnesium sheet showed a black deposit at and near the spot welds and was visibly corroded in the blackened areas. The spectrographic examination revealed that the blackened areas bore substantial amounts of copper, which would be expected to cause corrosion. The technique used is a rather typical example of the application of spark methods to such problems. A spark discharge from a pointed graphite rod was played on the blackened surface for a few seconds and the spectrum produced was compared with one produced by an unblackened portion of the surface of the same specimen. Figure 6 shows portions of the spectrograms obtained. The first spectra is an iron arc reference spectra. The second, fourth, sixth, and eighth spectra represent blackened areas of the sheet, and the third, fifth, seventh, and ninth each represents an unblackened area adjacent to the blackened area represented by the preceding spectrum. The copper originated in the spot-welding electrodes and it was subsequently found that both the blackening and the corrosion were easily avoided by scratch-brushing the surface after spot-welding.

Identification of Platings and Coatings. The identification of very thin platings or coatings is an occasional problem in most laboratories and a very frequent one at Aluminum Research Laboratories. A rather typical example is afforded by a sample recently submitted by an inventor who claimed to have a remarkable and mysterious method for plating aluminum on steel from an aqueous solution.

The specimen submitted was a piece of sheet about 1 inch square, very thinly coated with a light-colored metal. Visual examination of a scraped area indicated that the base metal was copper or brass and not steel. The coating and core were positively identified by subjecting them to a weak spark discharge. The spectra revealed that the specimen was simply high-grade copper sheet, bearing a thin coating of tin. Portions of the spectrograms obtained are shown in Figure 7. In this figure, the first spectrum represents the core metal, and the second represents the plating plus a certain amount of the core, unavoidably included because of the thinness of the coating.

While the spark technique is generally used in identifying coatings on metal surfaces, it is usually necessary to employ the direct current arc in studying coatings on other materials.

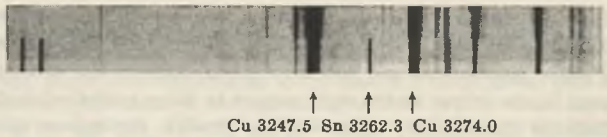

Figure 7. Spark Spectra of Core and Coating of Tin-Coated Copper Sheet

For example, this laboratory was recently asked to assist in identifying the transparent coatings on two samples of glass which showed appreciable electrical conductivity. Each coating was removed by leaching briefly with hydrofluoric acid, cleaned by further leaching, and then leached for the purpose of obtaining a blank. The leaches of the coatings and blanks were evaporated to dryness and the residues compared by means of arc spectra. One of the surfaces tested was found to be very high in rhodium and the other high in tin. Figure 8 shows the spectra on which these analyses were based.

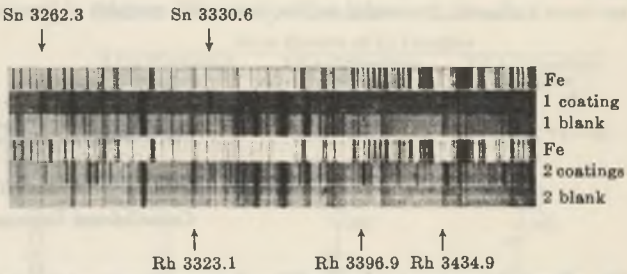

Figure 8. Arc Spectra to Determine Nature of Electrically Conducting Coatings on Glass

Miscellaneous Applications. Following are a few examples, taken from the files of Aluminum Research Laboratories, which illustrate the diversity of problems in which emission spectroscopy has been useful:

Particles weighing 0.01 mg. or less have been identified as to major metallic constituents by means of arc spectra. In many cases the particle was so small that it was necessary to handle it under a microscope. Such samples are usually placed in a graphite electrode and covered with a layer of powdered graphite to avoid losing the sample before it can produce its spectrum.

By simple arc techniques, the analytical chemist can often determine which of several brands of a reagent is most suitable for a particular determination and can often trace contaminants which may cause high blanks or interfering effects, directly to their source. Spectrographic tests of this sort have been valuable in the development of chemical procedures and in the selection of reagents in Aluminum Research Laboratories.

A large number of samples of sheet rubber were submitted to the laboratory to determine whether the zinc content was above or below a certain specification. A rapid spectrographic method of sufficient precision was devised by one of the chemists within the space of an hour. This method consisted of simply cutting a small disk from each sample with a paper punch and using this disk as one electrode in the spark. While rubber electrodes are not generally considered feasible, they performed very well in this application and the method has been adopted as a regular acceptance test. The rubber samples involved, both in the original work and in the subsequent routine work, were sheets about 0.125 inch thick. At the start of the exposure the spark first jumps to the supporting electrode. The surface of the rubber is carbonized almost immediately and will then sustain the spark. The results obtained are reasonably reproducible and it was found practical to base the determination on duplicate spectrograms compared visually with spectrograms of a sample containing the amount specified as the acceptance limit. The results are dependable within about 15% of the amount present.

SUMMARY

While the scope and diversity of analytical methods based on emission spectrometry preclude anything approaching a comprehensive treatment in this paper, it is hoped that the general

discussion, coupled with the specific examples drawn from one general analytical laboratory, will indicate useful applications in other laboratories and will help in establishing the spectrograph in its proper status with respect to other analytical tools. Emission spectrometry alone will not provide the answer to a very large proportion of the problems presented to the laboratory and its limitations, as well as its advantages, must be recognized if the spectrograph is to be effectively applied in the analytical scheme. Although the spectrographic analysis of a sample may provide more information than any other type of analysis, it can rarely, if ever, be considered a complete analysis and must always be supplemented by other techniques if nonmetallic elements are of interest or if compounds must be identified or determined.

Quantitative spectrographic methods are feasible in many applications and in specific cases may be superior to any other existing method. However, such cases are the exception rather than the rule, and all precise quantitative spectrographic analyses must be based on careful calibrations with samples of known composition and must be preceded by careful investigation of sampling, excitation, and other factors pertaining to the specific analysis to be made. The automatic, push-button type of spectrographic procedure, in which a relatively untrained operator manipulates a few switches and levers and is presented with an accurate quantitative analysis, is possible only under very favorable circumstances and, as a rule, only after months or years of research and development.

Bearing these limitations in mind, the spectrograph is still one of the most useful pieces of apparatus in the modern analytical laboratory. While emission spectrometry supplants other methods of testing in particular cases, its most important contributions are in complementing other methods and in greatly increasing the amount of information the chemical analyst can glean from the samples he receives. The extent to which this combination of art and science contributes to the functions of the analytical laboratory depends largely on the initiative and imagination of the analyst, and on his background of training and experience in analytical chemistry.

Mass Spectrometry

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Consolidated Engineering Corp., Pasadena, Calif.

The observed experimental correlation between mass spectra and structure of hydrocarbon molecules is illustrated by the spectra of the octanes. The large variations of spectra with minor variations in arrangement of atoms in a molecule are responsible for the applicability of the mass spectrometer to analysis of isomeric paraffin mixtures containing as many as ten components. The analysis of a mixture from its mass spectrum can be obtained from the solution of linear simultaneous equations. However, in samples encountered in the C_1 through C_8 range of hydrocarbons, many components or groups of components can be determined from mass spectrum peaks which receive no contribution from other components in the mixture. This is especially true when the peaks referred to are corrected for the presence of heavy isotope. The resulting simplifications in computing the analyses are illustrated by specific examples. Some types of mixtures which are advantageously analyzed by the mass spectrometer are discussed. A short description of instrument operation is included.

THE mass spectrometer has in the past two years graduated from a piece of laboratory apparatus to an industrial instrument. It is at present being used for refinery control as well as for special analytical problems encountered in refinery operation, and is employed in experimental laboratories engaged in process development and other chemical research.

This paper gives a brief historical sketch of the subject and indicates the types of analyses to which this new analytical method is well adapted. In addition, its specific application to refinery control is described.

HISTORICAL SKETCH

The first mass spectrograph was built by Aston as part of a rather extensive research program to study the new gas at mass 22 observed on Sir J. J. Thomson's positive ray apparatus. When this gas was discovered in 1913, it was not known whether it was an unknown gas or an isotope of neon similar to Sardi's isotopes observed in the radioactive elements.

In 1920 Aston proved this gas was an isotope of neon by means of the mass spectrograph. Aston then carried on his searches to find the masses and relative abundances of the isotopes of some 58 of the elements. From these data he was able to determine the atomic weights accurately.

The mass spectrograph is an accurate instrument for determining the masses of the isotopes, but is not accurate in the determination of the relative abundances. This is due to the fact that in the mass spectrograph the spectrum is recorded by allowing ions of several masses to impinge simultaneously on a photographic plate, and the abundances are then determined from measurements of photographic density. To overcome the inaccuracies inherent in density measurements, an instrument was developed which recorded the abundances by allowing the ions of a single mass at a time to impinge on a target which was connected to an electrometer or to an electrometer tube and galvanometer. Because of this new method of recording, this instrument was named the mass spectrometer to distinguish it from the mass spectrograph.

The mass spectrometer is the simpler instrument of the two, since only a single mass at a time is recorded and high resolution is not required for recording relative abundance. This simplicity was partly responsible for the extension of the use of the mass spectrometer to fields other than the relative abundance measurements in the determination of atomic weights.

New applications at first were in isotope tracer experiments and in fundamental studies employing appearance potentials measured by the instrument. The most recent development is the improvement of the instrument which permits its application to the analysis of gas and liquid mixtures. It is this application of the mass spectrometer which is discussed in the present paper.

APPARATUS

The mass spectrometer and associated apparatus are shown in Figure 1. Either gas or liquid samples can be analyzed. If the sample is normally a gas, it is first introduced into the metering volume where its pressure is measured, then expanded into the inlet sample bottle.

If the sample is normally a liquid, a known amount of the liquid is first sealed in a small glass ampoule. This ampoule is waxed into the metal break-off compartment where it is broken off under vacuum and allowed to expand into the inlet sample bottle. The pressure in the inlet sample bottle is sufficiently low, so that the normally liquid sample is in vapor phase and hence for the remainder of its flow need not be distinguished from the gas sample.

The sample is allowed to flow through the ionization chamber by opening the stopcock immediately ahead of the orifice. The pumping system and orifice are so designed that a constant flow of the sample is maintained through the ionization chamber.

When in the ionization chamber, the gas is subjected to electron bombardment which converts some of the neutral molecules into positive ions. These ions are acted on by electric and magnetic fields in such a manner as to form a fan of ion beams, each beam containing ions of one mass only.

By gradually varying the electric or magnetic fields this fan of ion beams is forced to sweep past the exit slit, *E*. In this manner the ion beams are allowed to impinge successively on the target, *T*. The current imparted to the target is amplified and fed into a galvanometer which deflects through an angle proportional to the abundance of the ions in each beam.

The galvanometer deflections are recorded by passing a sensitized photographic paper at a uniform rate past the galvanometer light beam. The resulting record is called a mass spectrum.

From the mass spectrum of a mixture and a knowledge of the mass spectra of its components, the composition of the mixture can be determined. In order to explain the method of analysis it is necessary first to discuss the process of ionization.

IONIZATION BY ELECTRON IMPACT

The mechanism of ionization by electron impact of hydrocarbons has been definitely established only in a few very simple cases (*1*, *2*, *3*). It is, therefore, possible to make only a very general statement regarding the mechanism of ionization. Ionization occurs when the path of an electron comes sufficiently close to a neutral molecule so that the interaction of their fields causes the neutral molecule to absorb some energy from the ionizing electron. As a result of absorbing this energy, the molecule loses an electron, or it loses an electron and in addition breaks up into fragments. In general, then, there are obtained upon ionization a positive ion, a neutral fragment or fragments, and an electron.

The relative abundance of ions of different masses formed by the electron bombardment of any particular substance depends upon the relative probability of the different ionization processes. A qualitative idea of a few of the factors controlling the relative abundance of ions may be gained from a study of the mass spectra of the C_5, C_6, C_7, and C_8 paraffins.

Three C_8 paraffins of similar structure—namely, 2,2,3-trimethylpentane, 2,2,4-trimethylpentane, and 2,3,4-trimethylpentane—were chosen to demonstrate these factors and are shown in Table I.

For simplicity, the hydrogens have been omitted from the structural formulas shown at the head of each column. In these structures the asterisk indicates the bond which is broken in the most probable process of ionization. The plus sign indicates the next most probable process. The mass numbers for which ion abundances are shown are 114, which corresponds to the positive ions formed by the loss of an electron only, mass 99 corresponding to the loss of a methyl group plus an electron, mass 71 corresponding to the loss of a propyl group plus an electron, mass 57 corresponding to the loss of a butyl group plus an electron, and mass 43 corresponding to the loss of an amyl group plus an electron. The relative abundances of the ions are represented in the body of the table by numbers which are proportional to the abundance of the respective ions.

The most outstanding feature indicated by the relative abundances shown in Table I is that the most probable products of ionization are formed by the molecule breaking into two equal or nearly equal parts. This is illustrated by the relatively large size of the abundances at mass 57 of 2,2,3- and 2,2,4-trimethylpentane. In the case of 2,3,4-trimethylpentane the molecule cannot break into two equal parts without first going through an isomerization. The largest abundances in this case, therefore,

Table I. Products of Ionization of C_8 Paraffins

Mass Number	Mass Spectra of C_8 Paraffins: 2,2,3-Trimethylpentane	2,2,4-Trimethylpentane	2,3,4-Trimethylpentane
114	0.1	0.02	0.3
99	3	5	0.1
85	3	0.02	0.05
71	1	1	40
57	70	80	9
43	15	20	50

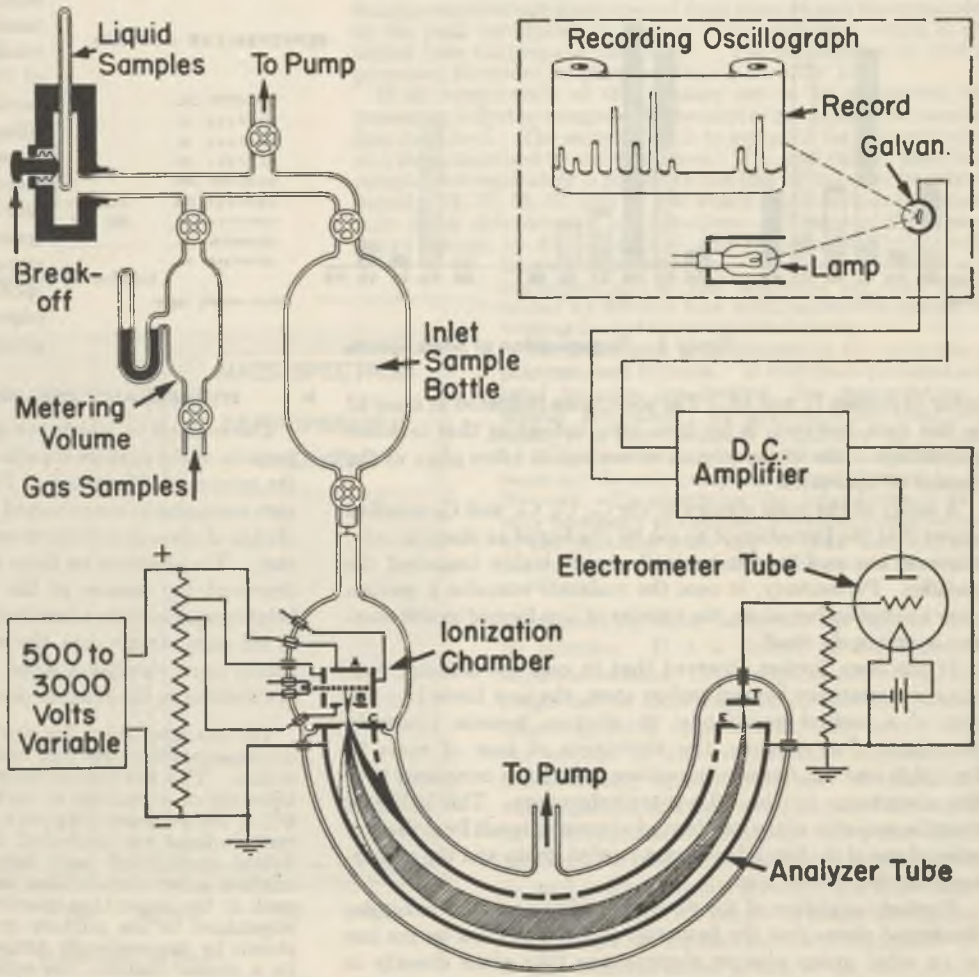

Figure 1. Diagram of Mass Spectrometer and Associated Apparatus

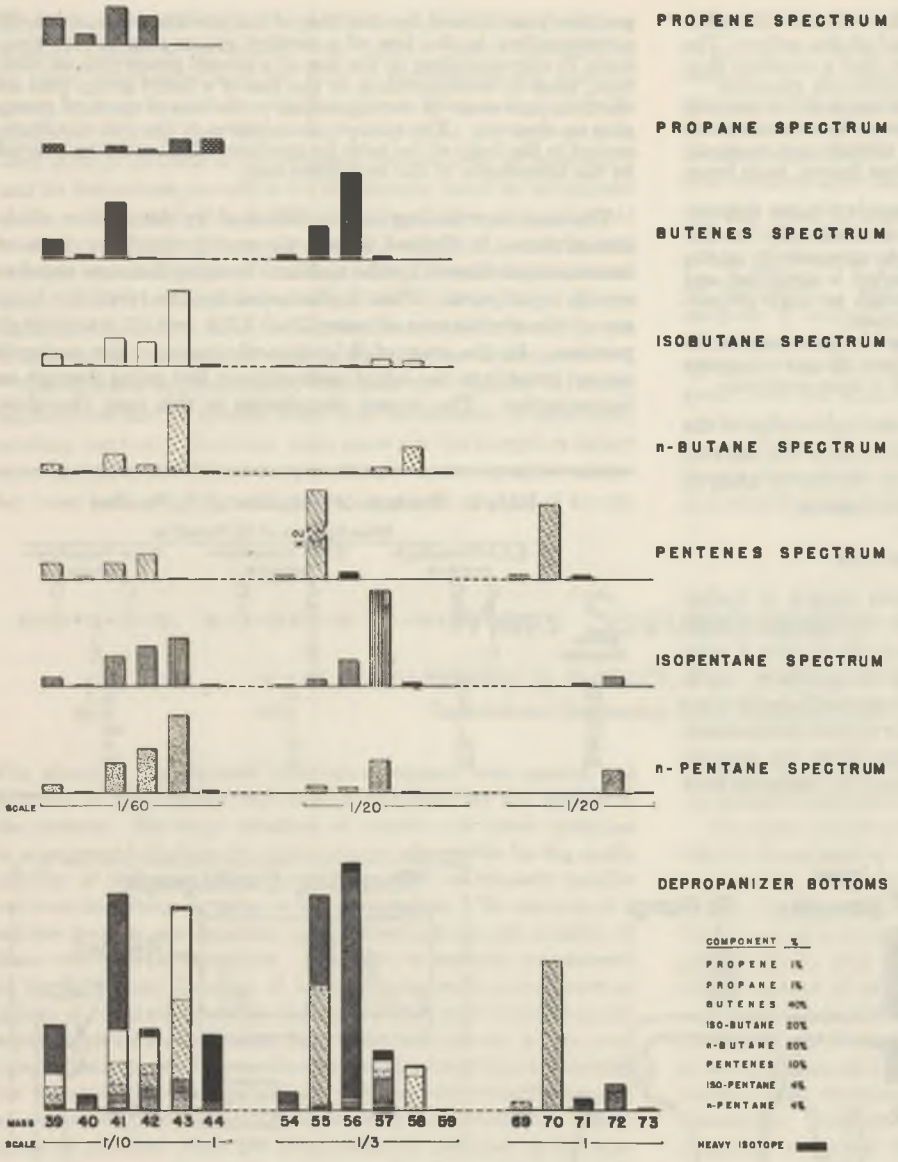

Figure 2. Superposition of Mass Spectra

occur at masses 71 and 43. The abundance indicated at mass 57 in this case, however, is far from zero, indicating that in a fair percentage of the ionizations an isomerization takes place at the instant of ionization.

A study of the mass spectra of the C_5, C_6, C_7, and C_8 paraffins shows that the formation of an ion by the loss of an electron only, becomes less and less probable the more highly branched the paraffin. Particularly, in case the molecule contains a quaternary bonded carbon atom, the number of ions formed in this manner is extremely small.

It has been further observed that in case the molecule contains a quaternary bonded carbon atom, the ions formed by the loss of a methyl group plus an electron become relatively abundant. For example, the abundance of ions of mass 99 for 2,2,3- and 2,2,4-trimethylpentane is large as compared with this abundance for the 2,3,4-trimethylpentane. This indicates that the majority of the ions formed at mass 99 result from the severing of one of the bonds between a methyl group and the quaternary bonded carbon atom.

Further inspection of the structures of the paraffin molecules illustrated shows that the formation of a positive ion by the loss of an ethyl group plus an electron can take place directly in 2,2,3-trimethylpentane, but requires an isomerization at the time of ionization in 2,2,4- and 2,3,4-trimethylpentane. As might be expected from this discussion, the abundance of the ions of mass 85 is relatively large for the 2,2,3-trimethylpentane as compared to the 2,2,4- and 2,3,4-trimethylpentane.

A comparison of the structures of 2,2,3- and 2,2,4-trimethylpentane suggests that the ions formed by the loss of a propyl group plus an electron should be more abundant for the 2,2,4-trimethylpentane, since the 2,2,3-trimethylpentane requires an isomerization at the time of ionization for this to take place.

However, the data indicate that this is not the case. A possible explanation is that the tendency for the molecule to break into two equal parts is so great that the formation of an ion by the loss of a propyl group from 2,2,4-trimethylpentane becomes less probable.

One of the important conclusions that may be drawn from the above discussion is that even though the structures of two molecules are similar, their spectra may be different. Furthermore, even though the exact mechanism of ionization is little understood, it is an experimentally established fact that the mass spectra obtained under constant conditions of ionization are functions of the structure of the molecule. A particular substance is therefore identified with a particular mass spectrum. As will now be shown, the one-to-one correspondence between a substance and its mass spectrum permits the determination of the quantity of that substance in a mixture from the mass spectrum of the mixture and a knowledge of the mass spectra of the components of that mixture.

SYNTHESIS AND ANALYSIS OF MIXTURE MASS SPECTRA

The method in which the mass spectra of the separate components of the mixture superimpose to form the mass spectrum of the mixture is illustrated in Figure 2. The spectra for the mixture components are obtained by introducing a standard pressure of each of these pure substances separately into the mass spectrometer. The abscissas on these mass spectra at which peaks occur represent the masses of the ions, and the ordinates or peak heights represent the abundances of the ions. From these spectra of the pure components, the mass spectrum which would be obtained upon running a given mixture can be predetermined or synthesized in the manner described below.

The mixture chosen for illustration corresponds to a sample of depropanizer bottoms and contains C_3 through C_5 paraffins and olefins. The mixture contains 4% *n*-pentane, and so the contribution of *n*-pentane to each peak in the mixture spectrum is 4% of the corresponding peak in the *n*-pentane spectrum. These contributions are indicated in the mixture spectrum by the dotted portion of each mixture peak. Similarly, since the mixture under consideration contains 4% isopentane, 4% of each peak in the isopentane spectrum will be the contribution of the isopentane to the mixture spectrum. These contributions are shown by the vertically striped portions of the mixture peaks. In a similar manner, the contributions of 10% pentenes, 20% *n*-butane, 20% isobutane, 40% butenes, 1% propane, and 1%

propene are indicated by cross-hatching of different types corresponding to the cross hatching of the respective pure component spectra. To sum up, the mixture spectrum is the linear superposition of the spectra of the pure components.

The analysis of a mixture, from the mixture mass spectrum and a knowledge of the mass spectra of the pure components in the mixture, consists of the unraveling of the mixture mass spectrum into its component parts or the reverse of the synthesis described above. The data are therefore the same as shown in Figure 2 with the exception that the peaks in the mixture spectrum would not be subdivided.

Since the above superposition is linear, the analysis for the separate components in the mixture can always be obtained by merely solving a set of simultaneous linear equations, the number of equations being equal to the number of components in the mixture. The data required to set up the simultaneous equations for an analysis of an N-component mixture are the heights of N mixture peaks and the heights of the peaks at these same masses in the calibration spectra. The details of setting up these simultaneous equations are given in a previous publication (*4*). It is, however, in practice seldom necessary to solve a large number of simultaneous equations, since in many practical cases the characteristics of the mass spectra are such that short-cut methods can be employed. For example, if the portions of the peaks due to heavy isotopes are segregated the analysis procedure is simplified.

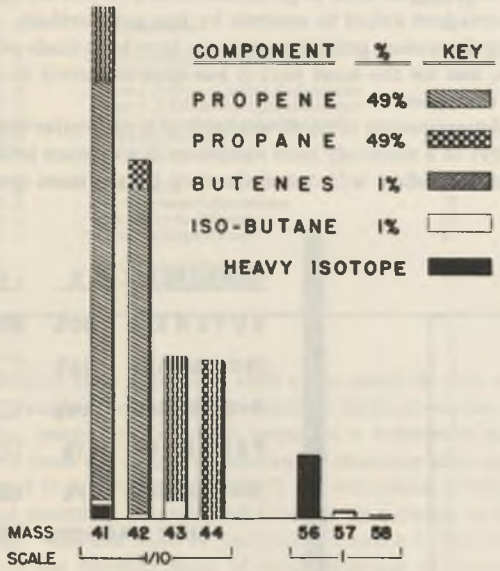

Figure 3. Depropanizer Overhead

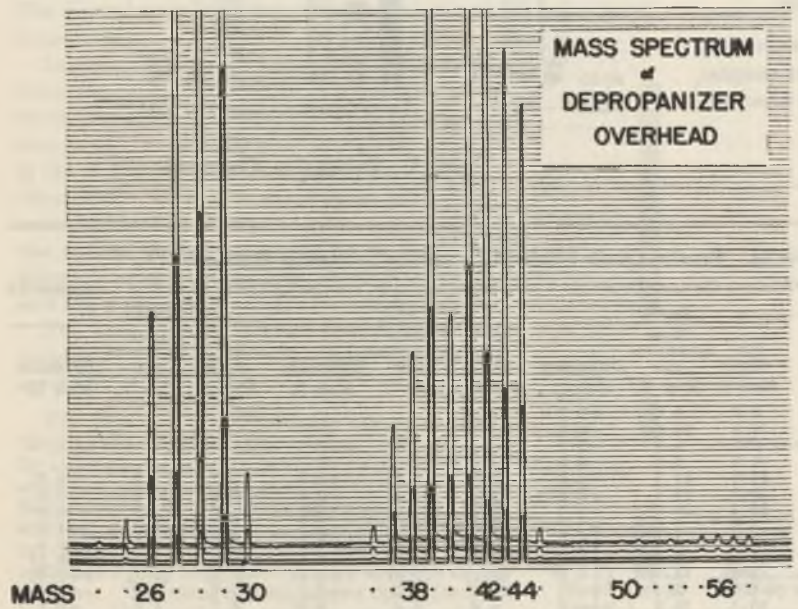

Figure 4. Automatic Record

Four galvanometers record peaks simultaneously at four sensitivity els to ensure accurate measurement over e large range of magnitudes.

In the mixture spectrum shown in Figure 2, the portion of each peak due to heavy isotope is indicated by solid black. For example, the black portion of the 44 peak is due not to ions of composition C_3H_8 but to C_3H_7 where one of the carbons is of mass 13 instead of mass 12, or one of the hydrogens is a deuterium. An inspection of the 43 peak shows that the major part of this heavy isotope contribution to the 44 peak is due to *n*-pentane, isopentane, *n*-butane, and isobutane. Fortunately, in nature the ratio of the heavy to light isotopes is substantially constant. The portion of the peak due to the heavy isotope can therefore be determined with sufficient accuracy by multiplying the peaks at the two adjacent lighter masses by constants which are determined from the ratio of heavy to light isotopes observed in nature. In this case, the correction is approximately 3% of the 43 peak minus 0.09% of the 42 peak. It is important to observe that the parent peak of propane at mass 44 and the parent peak of the butanes at mass 58 are not contributed to by the heavier hydrocarbons except for heavy isotope. This fact greatly simplifies the analysis of the mixture spectrum. The nature of this simplification and the time that is required to make the analysis are best illustrated by taking a few specific examples.

Analysis of Depropanizer Bottoms. The first example chosen is that of the depropanizer bottoms for which the synthesis shown in Figure 2 was described.

If the analysis is to be made for purposes of control it is necessary only to determine the amount of propane in the mixture. Figure 2 shows that this is an extremely simple determination, since the only component contributing to peak 44 other than heavy isotope is propane. To determine propane, the heavy isotope contribution is subtracted from peak 44 and the remainder of the peak multiplied by a sensitivity coefficient which is obtained from the propane calibration. The calculations for control purposes, therefore, require less than 5 minutes' time.

If all components of the mixture are to be computed, the procedure is first to compute the amount of propane in the manner just described. The second step is to compute the amounts of *n*- and isopentane and *n*- and isobutane. The analysis for these four components separately is possible since four or more peaks exist—namely, 72, 71, 58, 57, and 43—to which other components make only small determinable contributions. These contributions—heavy isotope to 43, 57, and 71 and propane to 43—are subtracted from the peaks. The amounts of *n*- and isopentane and *n*- and isobutane are then determined by solving four simultaneous equations involving four of these corrected peaks.

The third step is to determine the amounts of pentenes and butenes. If only total pentenes and total butenes are desired, the computation is greatly simplified. To determine the total pentenes, it is only necessary to multiply the 70 peak by the proper sensitivity coefficient, since the pentenes are the only components contributing to the 70 peak. To determine the total butenes, it is only necessary to subtract the small contributions of the paraffins from the 56 peak and multiply the remainder of the peak by the proper sensitivity coefficient.

In practice, these computations require about 30 minutes. If it is desired to determine the separate butenes, the computations are a little longer but no more complex and the computation time required is approximately one hour. Thus, the amount of time required for computing depends mainly upon the amount of information that is desired, and for control purposes the amount of time required is extremely short, less than 5 minutes. If time for introducing sample, running it, and pumping it out is added, the total time of obtaining results for control is about 25 minutes.

Analysis of Depropanizer Overhead. The second example shown is that of the depropanizer overhead (see Figure 3).

Table II. Errors in Mass Spectrometer Analyses

(Average errors obtained from repeat runs on a C_1–C_4 paraffin-olefin mixture are shown together with an error range which includes 90% of the cases.)

Components	Composition, Mole %	No. of Determinations	Average Error, Mole %	90% of Errors Less Than
Methane	15			
Ethane	20			
Propane	20	215	0.2	0.4
Isobutane	10			
n-Butane	8			
Propylene	10	43	0.2	0.5
Isobutene	7	43	0.4	0.7
Butene-1	5	86	0.7	1.4
Butene-2	5			
Total butenes	17	43	0.4	0.8

If the analysis is for control purposes, it is only necessary to determine the amounts of isobutane and the total butenes. The computation here is simpler than in the previous case. The amount of isobutane can be determined by multiplying the 58 peak by a sensitivity coefficient and the amount of butenes can be determined by multiplying the 56 peak by a sensitivity coefficient. To make a complete analysis, the amount of propane can be determined by multiplying the 44 peak by a sensitivity coefficient, and the amount of propene can be determined by multiplying the 42 peak by a sensitivity coefficient after subtracting the small contributions of the propane and isobutane.

Figure 4 shows the automatic record of the mass spectrum of a depropanizer overhead. The recording of this complete record requires about 3 minutes. The height of the 58 peak in this recording is approximately 0.9 division. The sensitivity for isobutane is 2.5, and 0.9 times 2.5 yields 2.3% isobutane. The 56 peak is approximately 1.4 divisions high and the sensitivity of 0.2 gives 0.28 or approximately 0.3% butenes in the mixture. The amount of ethane and propane can be determined from the 30 and 44 peaks after they are corrected for heavy isotope, and the amount of propene can be determined from the 42 peak after subtracting the contribution of the isobutane and propane. The total time from receiving the sample to obtaining the results in this case is 30 minutes for the control analysis and 40 minutes for the complete analysis.

ANALYSIS OF DEBUTANIZER OVERHEAD. The third example, shown in Figure 5, is the debutanizer overhead.

Control analysis in this case is very similar to that of a depropanizer overhead, the amount of isopentane being determined from the 72 peak and the amount of pentenes from the 70 peak. If a complete analysis is desired, the amount of *n*- and isobutane can be determined by solving two simultaneous equations involving the 43 and 58 peaks. The total butenes can be determined by multiplying the 56 peak by a sensitivity coefficient after subtracting the small contributions of the paraffins. The analysis time for the debutanizer is also extremely short.

The foregoing examples illustrate why the mass spectrometer is particularly well adapted to analyzing refinery plant samples, and why it is capable of giving exceedingly rapid results when control analyses are desired.

ACCURACY OF MASS SPECTROMETER METHOD OF ANALYSIS

In order to determine accurately the errors which may be expected in a particular analysis, it is necessary to run a large number of synthetic samples. Fortunately, we have available 43 analyses made on one particular synthetic mixture, the acceptance test mixture for the Consolidated mass spectrometer. The errors observed are a fair representation of the errors normally encountered in the analysis of this type of mixture.

The analyses were made on nine different mass spectrometers; in all cases except one, they include all the analyses made on each instrument on this particular synthetic mixture. In the one case excepted, the synthetic mixture was found to be in error as a result of an air leak which occurred during the process of synthesizing the mixture. The results of these analyses are shown in Table II. The first column shows the components of the mixture. The second column shows the approximate composition of the mixture. The fourth column shows the average error in mole per cent. In order to give an idea of the spread of the errors, a fifth column shows an outside error within which 90% of the results were included.

One important result of the compilation of these errors is that from them it has been possible to obtain some empirical coefficients which permit the prediction of accuracy on mixtures which have not as yet been run, but for which the mass spectra of the various components have been determined.

TYPES OF MIXTURES AND THEIR ANALYSIS BY MASS SPECTROMETER

A good deal of work has been done in analyzing synthetic samples of different types with the mass spectrometer. The field is, however, broad and the method relatively new, so that it is difficult at this time to generalize to any extent on the types of mixtures best suited to analysis by this new method. In the following discussion, general statements have been made wherever possible, but for the most part it has been necessary to discuss specific examples.

The determination of small amounts of a particular substance (impurity) in a relatively pure sample or in a mixture is in many cases accomplished with more accuracy by the mass spectrom-

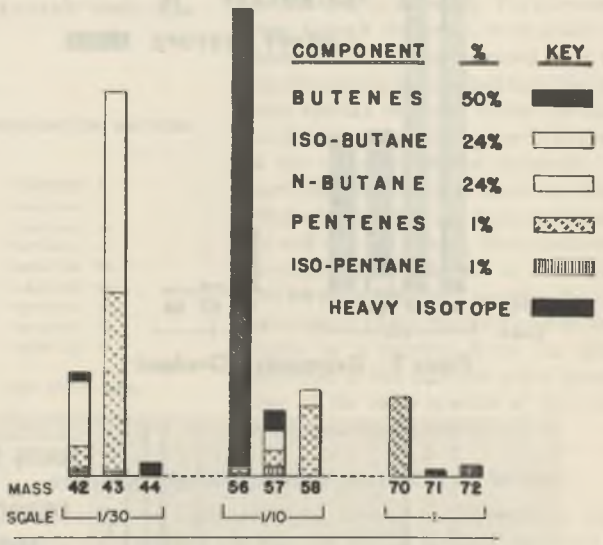

Figure 5. Debutanizer Overhead

Table III. Paraffin-Olefin Mixtures Containing Substantial Amounts of C_5's

(These mixtures illustrate the analysis of light hydrocarbon mixtures, containing a large number of components.)

	C_1–C_5			C_2–C_5			C_3–C_5		
	Synthetic	Mass Spectrometer	Difference	Synthetic	Mass Spectrometer	Difference	Synthetic	Mass Spectrometer	Difference
	Mole %	*Mole %*	*Mole %*	*Mole %*	*Mole %*	*Mole %*	*Mole %*	*Mole %*	*Mole %*
H_2	3.0	3.2	+0.2	..	..	...	..	..	...
Methane	10.8	10.3	−0.5	..	..	...	..	..	...
Ethylene	6.0	5.9	−0.1	..	..	...	..	..	...
Ethane	6.0	5.8	−0.2	..	..	...	..	..	...
Propene	11.1	11.1	0.0	12.5	13.1	+0.6	13.2	13.4	+0.2
Propane	19.2	19.5	+0.3	24.8	24.9	+0.1	25.9	26.4	+0.5
Isobutane	20.1	20.0	−0.1	25.0	25.0	0.0	25.6	25.6	0.0
Isobutene	2.8	1.6	−1.2	3.8	3.6	−0.2	4.1	3.0	−1.1
n-Butene	2.9	4.1	+1.2	5.4	5.3	−0.1	5.4	6.5	+1.1
(Butene-1)	(1.5)	(2.4)	(+0.9)	(3.0)	(2.6)	(−0.4)	(3.2)	(3.3)	(+0.1)
(Butene-2)	(1.4)	(1.7)	(+0.3)	(2.4)	(2.7)	(+0.3)	(2.2)	(3.2)	(+1.0)
n-Butane	5.0	5.2	+0.2	7.5	7.7	+0.2	7.6	7.8	+0.2
Isopentane	10.1	10.2	+0.1	6.4	6.4	0.0	6.7	6.5	−0.2
Pentenes	3.0	3.1	+0.1	8.2	7.5	−0.7	4.9	4.6	−0.3
n-Pentane	..	..	...	6.4	6.5	+0.1	6.6	6.2	−0.4

Table IV. Probable Accuracies in Determining Styrene and Butadiene in a Complex Mixture

Components	To Be Determined	Probable Mole % Accuracy Mixture 1 (70–80% sytrene)	Mixture 2 (55–85% butadiene)
n-Butane	..	...	...
Isobutane	..	...	...
n-Pentane	..	...	...
Isopentane	..	...	...
Total butenes	x	±0.3	±0.4
Total pentenes	x	±0.3	±0.4
Butadiene-1,3	x	±0.3	±1
Total C_5 diolefins	..	...	...
Styrene	x	±1	±0.1
Ethylbenzene	x	...[a]	...[a]
Vinylcyclohexene	x	...[a]	...[a]

[a] Information not available at present.

Table V. Paraffins and Naphthenes, C_7 Cut

B.P. °C.	Material	Composition Mole %	Approximate Average Error Mole %
80.8	Cyclohexane	0	...
87.5	1,1-Dimethylcyclopentane	5	1.5
90.1	2-Methylhexane	4	0.4
90.8	*trans*-1,3-Dimethylcyclopentane	...	...
91.9	*trans*-1,2-Dimethylcyclopentane	30	1.5
99.25	*cis*-1,2-Dimethylcyclopentane	...	...
92.0	3-Methylhexane	7	3.0
93.5	3-Ethylpentane	7	1.2
98.4	*n*-Heptane	15	0.9
99.2	2,2,4-Trimethylpentane	7	0.5
100.9	Methylcyclohexane	15	1.0
103.2	Ethylcyclopentane	10	0.5
106.0	2,2-Dimethylhexane	0	...
109.3	2,5-Dimethylhexane	0	...

eter method than is possible with other methods—for example, the determination of small amounts of diethylbenzene in ethylbenzene, pentenes in isoprene, pentenes or butenes in butadiene. In such cases the minimum amount of impurity that can be determined is approximately 0.01% for automatic recording. If manual recording is employed this can be reduced to less than 0.001%. Another case of particular interest to petroleum refiners is the determination of small amounts of pentenes and pentanes in a C_4 cut. In this case quantities of pentenes as small as 0.02% and of pentanes as small as 0.2% can be determined. For manual recording these values are less than 0.001 and 0.005%, respectively.

In general, where the impurity is of higher mass than the other components of a mixture, a very small amount of this impurity can be detected and measured. Frequently even though the impurity is not of heavier mass than other components of the mixture, some of its main peaks will occur at mass numbers to which the other components of the mixture do not contribute to an appreciable extent, if at all—for example, as small an amount as 0.2% of propane in a C_4 mixture can be detected.

The analysis of a mixture containing a large number of components is illustrated by the analyses shown in Table III.

The first mixture, containing hydrogen and C_1 through C_5 paraffins and olefins, was prepared by mixing together very carefully metered volumes of known and relatively pure hydrocarbons. The first column shows the mole per cent of each constituent in the mixture as determined during its synthesis. The second column shows the results obtained by the mass spectrometer analysis of the mixture. The third column shows the differences between the synthesis and the mass spectrometer determinations. These differences compare very favorably with the errors shown in Table II for C_1 through C_4 analyses. A great deal cannot be said regarding the accuracy of analyzing a particular type of mixture from one analysis; therefore, the method of predicting the accuracy which was previously mentioned was applied to this particular mixture, and the above comparison substantiated.

The predicted accuracies show that the average error in determining the paraffins in the C_1 through C_6 mixture is approximately the same as the errors in determining the paraffins in the C_1 through C_4 mixture, and that the average error of determining the separate olefins is roughly 50% larger than the errors of determining the respective olefins in the C_1 through C_4 mixture. It is found that the lumped C_5 olefins in the C_1 through C_5 mixture are determined with an average error approximately 50% greater than the lumped C_4 olefins in the C_1 through C_4 mixture. An additional prediction is that if *n*-pentane had been included in the C_1 through C_5 synthetic mixture illustrated, the accuracy of determination of the other components in the mixture would have been unaffected.

On pilot-plant samples small amounts (up to 0.3%) of C_6 can be tolerated in a C_1 through C_5 sample, provided proper corrections are made for their presence. Since the accuracy of the corrections depends upon the constancy of the composition of the C_6 portion, more than 0.3% C_6 is permissible when the samples are taken from full-scale refinery units. Satisfactory results have been obtained on samples containing up to 3% C_6.

The time of analysis is, of course, highly important. It has been found in practice that mixtures of this type require a total of about 2.8 man-hours per sample, including the time of running the sample, a pro-rated time for calibration, the time of computing the sample, and a pro-rated time for maintenance on the instrument. The time required to obtain the data—that is, the instrument time—is only 25 minutes.

Many times it is possible to make analyses for particular components in a mixture which contains so many components that complete analysis is impractical. An example of such an analysis is shown in Table IV. This mixture contains butadiene-1,3, C_4 paraffins and olefins, C_5 paraffins, olefins, and diolefins, and in addition, styrene, ethylbenzene, and butadiene dimer. This is an extremely complex mixture, but it so happens that the constituents of most interest can readily be determined. The accuracies with which they may be determined by the mass spectrometer method are shown in columns 2, 3, and 4. Such an analysis requires approximately 25 minutes' instrument time and about 1.5 hours' computing time. To these times should be added approximately 1.5 hours for sample preparation, which is necessary for gas-liquid samples which are not analyzed for all components.

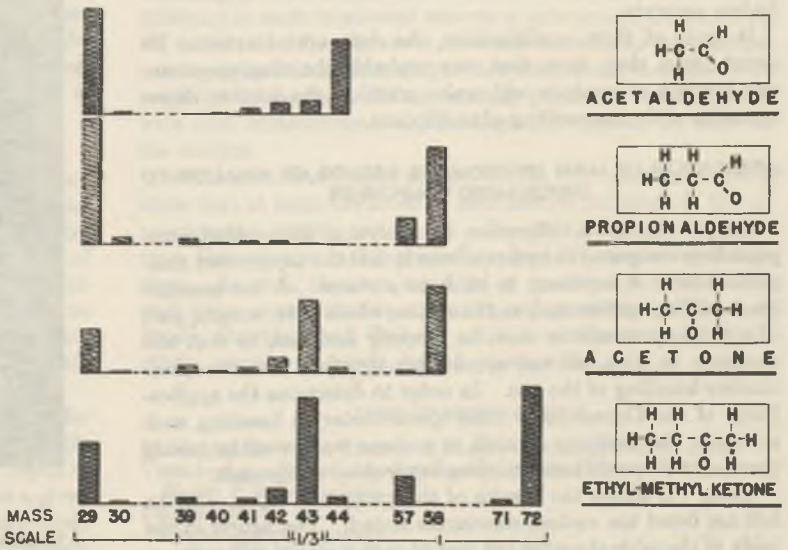

Figure 6. Spectra of Oxygenated Compounds

A mixture containing a large number of compounds of approximately the same mass is illustrated in Table V. This mixture contains all the C_7 naphthenes and the paraffins falling within the same boiling range. The column labeled "Approximate Average Error" shows the predicted accuracy for the analysis of a mixture of about the composition shown in the adjacent column.

To obtain more accuracy, it may be desirable in this particular mixture to divide the sample in two parts by fractionation. The cut would be made between 3-ethylpentane and *n*-heptane which have a 4.9° difference in boiling points. This method of handling would have the added advantage that some of the paraffins boiling in the range of 103.2° to 110° C. could be included in the heavy cut. In addition the *cis*- and *trans*-1,2- and the *trans*-1,3-dimethylcyclopentanes can very probably be individually determined.

The mixture does not contain *cis*-1,3-dimethylcyclopentane. Whether or not it will be necessary to lump the *cis*-1,3-dimethylcyclopentane with one of the other dimethylcyclopentanes or whether it will interfere with the separation between 1,2- and 1,3-dimethylcyclopentanes cannot be determined until a sample can be obtained in a pure state for calibration purposes.

Table VI. Estimated Accuracy of Mass Spectrometer Analysis of a Sample Having a Composition Similar to Aviation Alkylate

Material	Composition *Mole %*	Approximate Average Error *Mole %*
2,2,4-Trimethylpentane	56	±1.7
2,3,3-Trimethylpentane	14	±1.1
2,3,4-Trimethylpentane	14	±0.7
2,4-Dimethylhexane	6	±0.8
2,5-Dimethylhexane	6	±0.5
2,2,3-Trimethylpentane	4	±1.6

A second mixture containing several isomers is illustrated in Table VI. The mixture shown approximates the composition of the output from an alkylation unit except that it does not include any 2-methyl-3-ethylpentane, nor does it contain any C_7 or C_8 paraffins. This mixture, in common with those shown in Tables IV and V, was not run on the mass spectrometer but the separate components were. The accuracy of analyzing such mixtures with the mass spectrometer was estimated from the mass spectra of the pure constituents and the empirical error constants obtained from runs of synthetic C_1 through C_4 and C_4 through C_8 mixtures.

If an analysis is to be made of an alkylate, the alkylate should go through a preliminary fractionation to remove the C_7 or C_8 components at least to the extent where there are only about 10 components remaining in the mixture. The only disadvantage in having in the mixture 10 components instead of the 6 shown is that the computation time will be longer and the analysis will be less accurate.

In spite of these qualifications, the data are of extreme interest, since they show that very probably the mass spectrometer method of analysis will make practical the routine determination of the composition of an alkylate.

APPLICATION OF MASS SPECTROMETER METHOD OF ANALYSIS TO OXYGENATED COMPOUNDS

One of the main differences in analyzing oxygenated compounds as compared to hydrocarbons is that the oxygenated compounds have a tendency to stick to surfaces. A low-pressure gas-handling system such as the system which is an integral part of a mass spectrometer must be properly designed, so that this tendency to stick will not appreciably interfere with the quantitative handling of the gas. In order to determine the applicability of the Consolidated mass spectrometer to handling such mixtures, the tendency to stick to surfaces was tested by taking pump-out curves on some fourteen oxygenated compounds.

Table VII shows the results of the pump-out tests. On the left are listed the various substances tested. The figures in the body of the table show the per cent of each material still registering its mass spectrum after 1 minute and 5 minutes of pumping,

Table VII. Oxygenated Compounds

Material	Percentage of Material Remaining after Pumping 1 min.	5 min.
n-Butane	0.08	0.0
Formaldehyde	0.09	0.03
Acetaldehyde	0.16	0.11
Propionaldehyde	0.20	0.06
Dimethyl ether	0.25	0.0
Diethyl ether	0.23	0.04
Methyl formate	0.19	0.07
Acetone	0.28	0.06
Ethyl methyl ketone	1.43	0.52
Acetic acid	2.24	0.27

respectively. All substances shown appear to be satisfactory. The same tests were run on four alcohols but the results were contradictory within themselves. Representative data on alcohols therefore cannot be given at this time.

The present status is that the oxygenated compounds shown can be handled in the standard manner on the mass spectrometer. The remaining question which must be answered regarding the oxygenated compound is—do their mass spectra show sufficient resolution to permit accurate analyses? Figure 6 gives the mass spectra of four oxygenated compounds. These show definitely that there is excellent resolution, which in turn will give accurate analyses. The mass spectra of the other materials run also show excellent resolution.

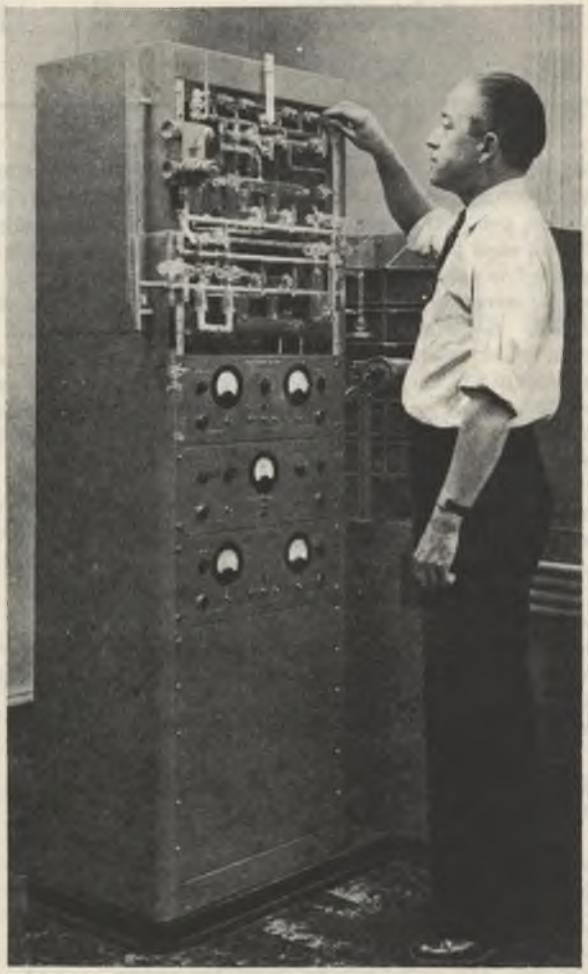

Figure 7. Sample-Introduction Apparatus

Sample bottle hanging on lower left of glassware contains a gas sample being introduced. Directly above bottle is metal system used for introducing normally liquid samples. Controls on panels below glassware operate vacuum gages and evacuation pumps.

The preceding discussion demonstrates that the mass spectrometer can very probably be used successfully in industry for the analysis of mixtures composed in part or entirely of oxygenated compounds. A more definite statement in this regard awaits the practical test of continued operation on such mixtures over a considerable period of time.

INSTRUMENT OPERATION

The routine operation of the mass spectrometer has worked out in practice to be a relatively simple procedure. The first operation is the handling of the sample. Figure 7 shows the gas-introduction apparatus. Samples are introduced into this system using techniques which are commonly employed in gas-handling apparatus described in first section of this paper.

The introduction procedure is completed by opening the stopcock between the inlet sample bottle and the mass spectrometer (allowing the sample to start flowing through the mass spectrometer). After this operation one minute is allowed for the gas flow to come to equilibrium. During this short period of time, the operator checks the various voltages supplying the mass spectrometer. In particular, he checks the value of the positive ion accelerating voltage to make certain that he will start at the lowest mass which he desires to record.

At the end of this one-minute interval he pushes the mass marker reset button, turns on the camera switch, and throws the sweep switch to the sweep position. The mass spectrum is then recorded automatically and the operator merely checks once or twice on the instruments during the run and if necessary corrects any slight variation that may occur. The recording of the records takes from 5 to 10 minutes, depending upon the range of masses which it is desired to record. If the operator wishes, he may keep a rough check upon the progress of the record by watching a meter which is in series with the galvanometers.

As soon as the recording is completed, the photographic paper is removed from the camera and taken to the dark room with the aid of a light-tight sleeve. The developing, fixing, and washing processes require less than 5 minutes, which is approximately the time required for pumping out the sample so that the next sample can be introduced. The majority of the water is removed from the record with a sponge and the record is then ready for analysis.

CONCLUSION

This paper has dealt for the most part with applications to the petroleum refinery. The data presented show that the mass spectrometer has proved to be of definite value in this field as a relatively speedy, accurate, analytical tool. The method described is, however, a general one and is at the present time just beginning to be applied to other fields in the chemical industry. It is the authors' aim to continue development of the method for application in all fields where it shows promise of aiding in the solution of important technical problems.

ACKNOWLEDGMENT

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Light Absorption Spectrometry

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The analytical applications of light absorption spectrometry involve determination of the absorptive capacity of materials for radiant energy in the wave-length range of 400 to 750 mμ. These are the wave lengths which produce the sensation of light in the human eye. Since selective absorption results in color, when the unabsorbed radiant energy reaches the eye, this kind of method may be considered as a type of colorimetry. The uses of such absorptive measurements may be grouped into two general categories. Qualitative uses depend upon the kind of absorption—that is, the nature and contour of the transmittance–wave-length curve. In colorimetry this involves the hue of the system. Quantitative uses depend upon the intensity of absorption—that is, the height of the characteristic portion of the curve. In colorimetry this involves luminance and purity, which in turn depend upon the amount of the absorbing constituent present.

ABSORPTION spectrometry deals with the determination of the absorptive capacity of a given system for radiant energy. The subdivision limited to light absorption includes the wave lengths capable of producing the sensation of light in the human eye. This visible region, covering approximately 400 to 750 mμ for a normal observer, lies between the ultraviolet and the infrared regions. In this symposium we are concerned with the chemical applications of the subject, with particular reference to its place in testing and analysis.

In a general way light absorption spectrometry does not differ essentially from ultraviolet or infrared spectrometry, especially in the nature of the experimental data. Whatever the region of the spectrum, these data are single absorptive values for a given wave length, curves for a range of wave lengths, or, more rarely in recent years, photographic data for some region. Unless monochromatic sources are used to provide radiant energy of particular wave lengths, any stated wave-length value is usually the median of a spectral band whose width depends upon the instrument.

Presumably our first concern is with the means and methods available for securing the data, together with the manner of handling or presenting the information. Next in importance, for this symposium at least, is the application of the data.

INSTRUMENTS AND DATA

Since a general discussion of instruments cannot be presented, reference is made to selected sources of information (*7*, *22*, *23*, *24*, *37*, *39*, *55*, *80*, *85*). However, it seems desirable to mention certain aspects of the relationship of instruments and their use to the reliability of the data. Many recently published articles dealing with such measurements are inadequately written, at least for the analyst.

As far as measurements themselves are concerned, suffice it to state that at least the kinds of instruments indicated in the accompanying outline are in use. Except for the photographic type, they are now rather generally referred to as spectrophotometers. As such, they are one kind of spectroradiometers. For each type representative examples are mentioned. Those of Brode, Harrison, and Zscheile are not on the market. Many others, varying in details, have been described.

TYPES OF INSTRUMENTS

Photographic—e.g., Bausch & Lomb, Gaertner, Hilger, Zeiss
Visual—e.g., Bausch & Lomb, Gaertner, Hilger, Keuffel and Esser, König-Martens
Photoelectric
  Prism monochromator
    Nonrecording—e.g., Beckman, Zscheile
    Recording—e.g., Brode, General Electric

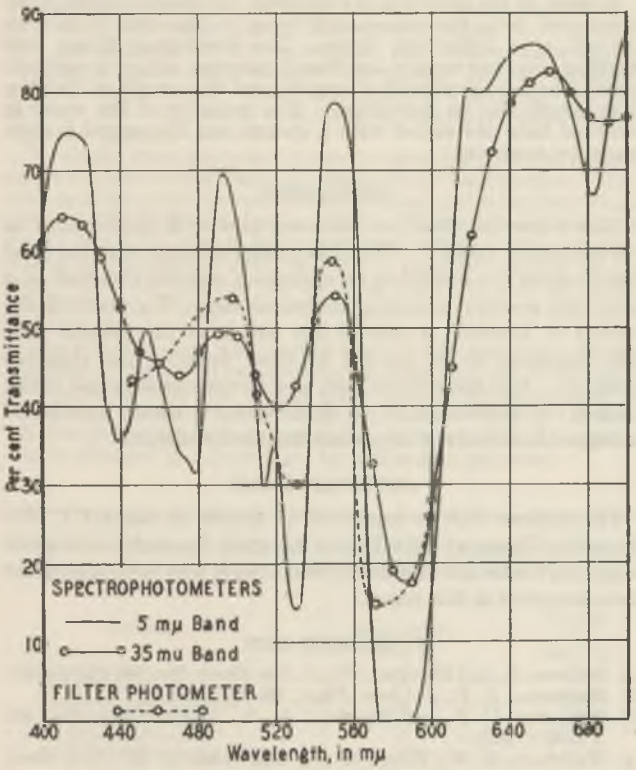

Figure 1. Transmittance of Corning Glass 512

Grating monochromator
Nonrecording—e.g., Coleman, Central Scientific
Recording—e.g., Harrison

The measurements may be considered, of course, as one type of colorimetry (*46*), since the sensation of color is related, in most cases, to the selective reflection or transmission of light by an object. Perhaps this is the most distinctive feature of light absorption spectrometry, for only in this subdivision do we have visual instruments.

Instrumental Details. Turning now to the evaluation of absorption data, one is interested first of all in their reliability. Since different instruments, and different methods of using them, may yield different results, reports of the details of measurements must be clearly and accurately written. Failure in this point indicates ignorance or laziness on the part of the authors. It is analytically inadequate, for example, to state only that the results were obtained by some individual, or that they came from some individual's laboratory.

In the first place, one wants to know the type of instrument—that is, whether it was photographic, visual, or photoelectric. Each type includes instruments of different qualities. If a photographic instrument was used, one may want to know whether any point matching of lines was done visually or by photoelectric means. An estimate of the probable reliability of the readings would help. Perhaps most important is to know whether a visual type was used, and, if so, with what light source. Values obtained visually for wave lengths below 440 or above 680 mμ are likely to be much less reliable than those near the center of this region because of the nature of the response of the eye to light. In addition to stating the type of instrument, authors should report the manufacturer and model. Thus, Coleman Model 10S will operate on a spectral band as narrow as 2.5 mμ, but that for Model 11 is 35 mμ.

Current papers seldom mention calibration. Recently the author found an error of 10 mμ (at 700 mμ) in a new spectrophotometer. It seems necessary to check both wave-length and photometric scales. Monochromatic sources, such as lines of the mercury arc, are preferable for checking wave lengths. Band peaks of didymium glass (see Figure 1) are useful for checking the wave lengths of recording spectrophotometers, if calibrated at the slit widths at which they are to be used; but they are much inferior to monochromatic sources for manually operated instruments. Glass standards of spectral transmission, calibrated by the National Bureau of Standards (typical curves are illustrated in Figure 8), are very useful for checking photometric values. Several solutions have been suggested for this purpose (*14, 72, 83*).

For curves having small, sharp bands (fine structure), the significance of spectral band width seems often not appreciated or understood. Many authors do not state the width used. Figure 1 shows the results of using different band widths for a didymium glass. The continuous curve, without points, was recorded with a band of 5 mμ, while that with the marked points is based on readings with a band of 35 mμ. The discontinuous curve is drawn through points marking the values obtained on a visual filter photometer using glass filters whose median wave lengths were stated by the manufacturer to be the values locating the points on the graph. The disagreement is obvious. In general, the use of a wide spectral region obscures or eliminates small bands which might well be the characteristic information sought. Two recent publications, from well-known laboratories, contain curves with no sign of the small bands known to be in the permanganate curve near 490, 508, 526, 545, and 567 mμ (*27*) (see Figure 6).

If a narrow spectral band width was used for these permanganate curves, perhaps too few points were taken to locate the curve. Unless data come from a recording instrument, the observed points should appear in the graph. This practice is by no means the rule today. Unless the curve is a broad, sweeping type, photometric readings should be taken at least each 10 mμ. To bring out small absorption bands, the points must be closer. Figure 2 shows the variation in the curves obtained by plotting the readings taken at different wave-length intervals for the glass used in Figure 1. It is evident that too few values can lead to serious inaccuracy for such a curve.

Along with pointless curves, one sees too many gridless graphs. The grid lines, because of their aid in studying and using curves, are recommended in books dealing with graphical presentation of data (*3, 89*).

If one wants to repeat another's work, it is very disconcerting to find no mention of the concentration of a solution or of the thickness of sample measured. For the sake of easy comparison of data—generally, absorption cells 1.00 cm. thick, or some multiple or fraction thereof, are preferable. But if the actual thickness is given, whatever it is, Bouguer's law enables one to calculate to any other thickness. A Keuffel and Esser color slide rule facilitates the work. Just as with wave-length and photometric scales, absorption cells should be checked. One lot of "1-cm." cells was found to range in internal thickness from 0.93 to 1.04 cm.

Data and Conventions. If one has an instrument capable of providing results of the desired accuracy, and if it has been adjusted and calibrated, there remains the question of how to handle the experimental data obtained. Only brief mention can be made here of methods of presentation, and this is limited to the construction of curves.

Although the terms absorptometric and absorptance are often used, more often the measurements are reflectance, R, for an opaque material, and transmittance, T (or transmittancy, T), for a transparent system. Reflectance is generally expressed as percentage. This basis is often used also for transmittance of solids and transmittancy of solutions. Hardy (*28*) and others prefer the decimal fraction, transmittance (or transmittancy) factor. Also there is extensive use of the optical density, D (designated often as extinction, E), the specific extinction, k, the molecular extinction, ϵ, or the logarithm of one of these. A number of instruments read directly in terms of one or more such values. Whatever the basis of the readings, they form the ordinates for curves. The region of the spectrum measured forms the abscissas, and the values are expressed in one or more of the following terms: wave length, λ (in millimicrons, mμ, or Ångströms, Å),

frequency, ν (in fresnels), wave number, ν' (in waves per cm.), and logarithm of the wave length. Brode (*7*) gives relationships and tables for interconversion of these values. From the standpoint of the accuracy of the measurement, few graphs would seem to justify the significant figures implied in using Ångström units.

Unfortunately, no one system of plotting has been generally adopted. Thus, a recent publication uses six different ordinate designations. This situation is the result partly of personal inertia and prejudice, and partly of the inadequacy of any one system for all requirements. With all possible variations in use, including inconsistency in the direction of plotting for any given combination, and disregard for good practice in graphing, the literature is likely to be confusing to one unskilled in transforming mentally a curve in unfamiliar form over into the form with which he customarily deals. Some advantages of several forms may be noted.

1. Transmittance (or transmittancy) is often the quantity obtained directly, especially with single-beam, substitution, or recording types of photoelectric instruments. Thus, presentation of the original data becomes easy. Since the light transmitted (reflected) determines the color, this kind of plotting is preferred by many in the designation of colors. Also, curves in this form are the basis for calculating numerical color specifications, as noted under Color Analyses, below. Some writers plot log T on equal-division paper, or T directly on semilogarithmic paper. Either method greatly magnifies values below 10%, but there is a corresponding condensation for high values.

2. Extinction, or optical density, magnifies absorption maxima, and thus makes them definite and easily read. It also facilitates computation from one thickness to another, if desired, since the relation is linear.

Curves of the percentage–wave-length or extinction–wave-length type often differ considerably in shape for different thicknesses of media or different concentrations of solutions. If one plots log E, the curves all have the same shape (*28*) regardless of thickness (or concentration, if the solution conforms to Beer's law). This is evident from the relation

$$E = \log_{10} 1/T = 0.4343\ kx$$

Then $\log_{10} E = \log_{10} 0.4343\ k + \log_{10} x$. Since the absorption coefficient, k, varies with the wave length and the thickness (or concentration) of the sample, x, does not, the shape of the curve depends upon the term $\log_{10} 0.4343\ k$, and the height upon the term $\log_{10} x$.

In some laboratories the latter type of curve is used for standard curves and for the identification of materials. In dyestuff manufacture and application, for example, the trade thinks in terms of shade and strength, variables immediately separable by this method as curve shape and position variations, respectively. Shurcliff (*69*) has proposed a curve-shape index for identifying dyes by means of spectrophotometric curves. For reflectance data, ordinate is $\log \frac{(1-R)^2}{R}$ in which R = body reflectance (*1*).

3. In theoretical and interpretative studies on the relation of absorption and constitution, often including the ultraviolet and infrared regions, frequency is of more fundamental importance than wave length as abscissas, since it gives a better indication of the relative widths of bands in the three regions. Shurcliff (*70*) prefers to use the logarithm of the wave length (to the base 2).

As another point concerning data, mention may be made of uncertainty in definition, and inconsistency in use, of the terms involved. Thus, unless one knows the solution measured, he cannot be sure that a curve labeled absorptance, in percentages, is not really a transmittance curve. Does a writer mean transmittance (ratio of transmitted to incident light) or transmittancy (ratio of transmittance of solution to transmittance of solvent)? When extinction is used, does he mean measured, specific, or molecular extinction? And in any case, has he specified concentration and thickness? When the ordinate is marked log E, does he mean a double log of $1/T$? Brode (*7*) and Gibson (*24*) have recommended uniformity in these items.

Finally, note may be taken of what seems unjustified faith in published extinction values, including their use in plotting curves intended either for measuring amounts of constituents or for demonstrating the applicability of Beer's law to the system. Ideally, a molecular extinction coefficient should be a physical constant comparable in reliability to other constants, such as density or refractive index. If the value is determined accurately, it may be considered reliable. But when one recalls that Beer's law presupposes monochromatic light, and that few spectrophotometers, as generally used, come near meeting this requirement, the discrepancies reported are understandable. Often a point of doubt is the purity of the material measured. Perhaps this too implicit faith in extinction values accounts for many authors' insisting on publishing extinction-concentration graphs for their particular work. If the line is straight, one sentence will so state. An experienced worker would not use the curve for another instrument without checking. An illustration of the significance of this instrumental factor has been published by Withrow, Shrewsbury, and Kraybill (*87*). Sandell (*66*) has wisely cautioned, "Only the most sanguine user of a spectrophotometer will calculate the concentration of his colored solution from the observed extinction and the value of the extinction taken from the literature." The dependence of extinction values upon conditions is shown by a statement such as $E(^{1\%}_{1\text{ cm.}}, 425\ \text{m}\mu, \text{CHCl}_3, 5\ \text{m}\mu, 20°\ \text{C.}) = 1800$.

APPLICATIONS

In general, the applications of light absorption spectrometry depend ultimately upon measuring color, a systemic property of increasing importance in research and industry. (The term color is not limited here to its psychophysical sense, recently defined, *11*.) Many chemical materials possess characteristic colors, or are subject to color changes in the course of chemical transformations. The range of applications extends from the determination of color as color, through the mass-production determination of desired constituents in routine laboratories, to the elucidation of chemical problems, such as those involving the constitution of systems, or the nature of processes.

The objective of the measurement differs widely (*7, 45, 47, 49,*

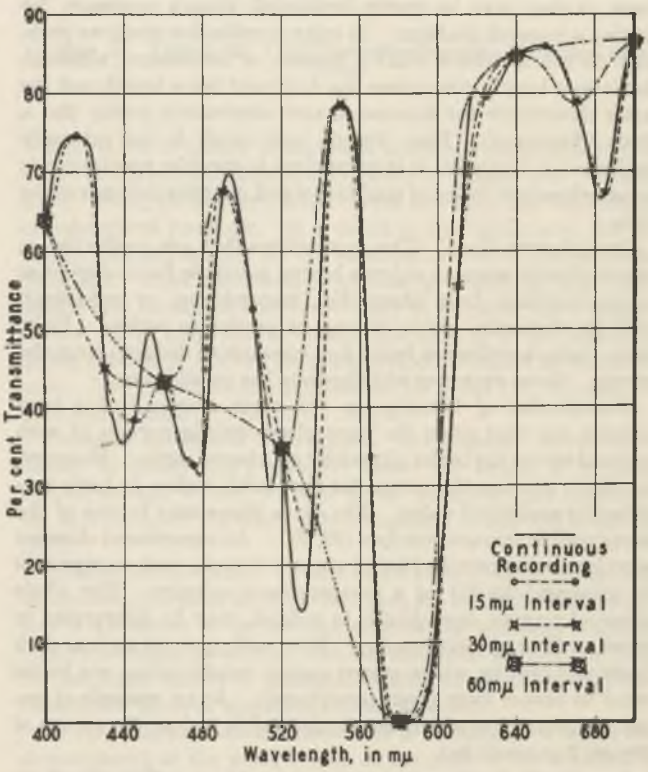

Figure 2. Effect on Curve of Wave-Length Intervals Plotted

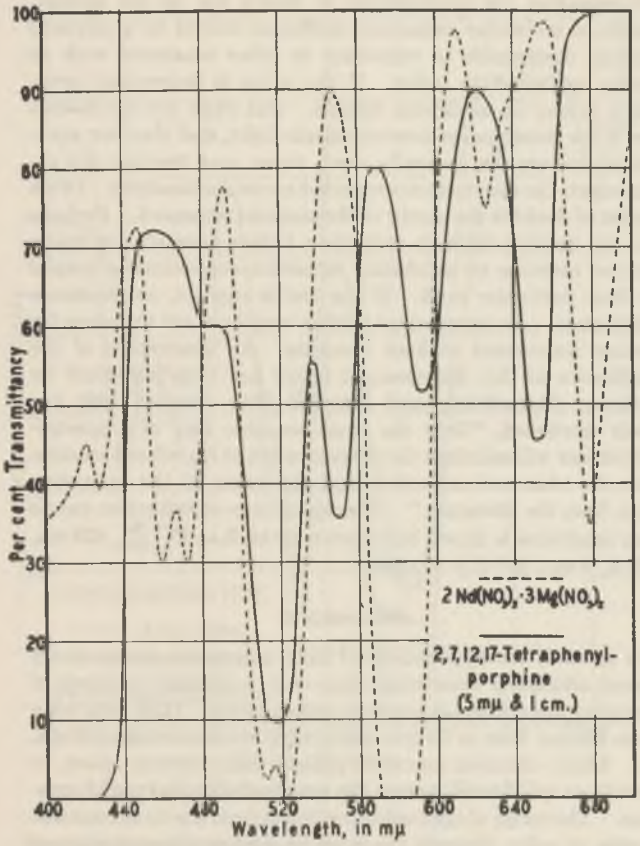

Figure 3. Characteristic Bands in Visible Region

54, 73). Perhaps most frequently it is purely analytical—that is, we want to know what constituent is present and/or its amount. Such determinations may be necessary industrial control operations, or they may be merely incidental, though necessary, for solving a research problem. In color specification work we probably do not determine what is present, or its amount, although the former largely determines the dominant wave length and the latter determines the luminance and colorimetric purity (for a given illuminant). Even though some work is not primarily analytical in objective, it is convenient to consider spectrometric measurements in terms of qualitative and quantitative uses of the data.

Qualitative Uses. The applications that are qualitative in nature depend upon an object's having a definite form of spectral curve (resulting from absorption, transmission, or reflection), with its distinctive parts, if any, in particular regions. Upon these characteristics are based any conclusions deduced from the curves. Some examples will illustrate the possibilities.

Identification of Constituents. In other sources it has been pointed out that often the most characteristic portion of such spectral curves lies in the ultraviolet or infrared region. However, for many systems the curves for the visible region do have considerable analytical value. The curve shape may be one of the items used to characterize dyes (*32, 67*). An experienced observer soon learns the peculiarities of a given system, such as pigments in printing inks (*1*) or a permanganate solution. The whole range of purples, from bluish to reddish, may be interpreted in terms of the respective curves. Even with systems such as dark blues and browns, whose curves appear uninteresting, one learns what to expect from given constituents. As an example of unusually interesting absorption in the visible region, the curves of Figure 3 are included.

In some work, where the curves do not have sufficiently sharp absorption maxima for such identification, it has been found preferable to use the ratio of extinction coefficients at selected wave lengths (*33*).

This use of curves has been very extensive in organic chemistry in studies involving correlation of absorption spectra and constitution of compounds (*6, 7, 8, 12, 15, 25, 29, 31, 49, 54*). If the curves for an unknown and a known agree closely, identity of composition or structure is indicated, but not confirmed, as noted by Ruehle (*64*), for two systems containing different substances may yield closely agreeing curves (*75*).

Spectrophotometric evidence on the nature and the course of chemical reactions belongs in this category. Such application, although probably most extensive in biochemistry and organic chemistry, is not confined to these subjects (*53*). Specific examples of these applications are papers on adsorption (*40*), complexation (*50*), hydrolysis (*9*), ionic equilibria (*5, 26, 63, 84*), ionization constants (*65*), isomerism (*61*), molecular association (*38*), polymerization (*62*), and solvation (*86*). To interpret the curves one should know the light absorptive effects of factors such as functional groups, specific structures, and possible chemical transformations (*30*). Change in hue, for given illumination, means a change in the nature of the absorbing system, although the reverse is not necessarily true.

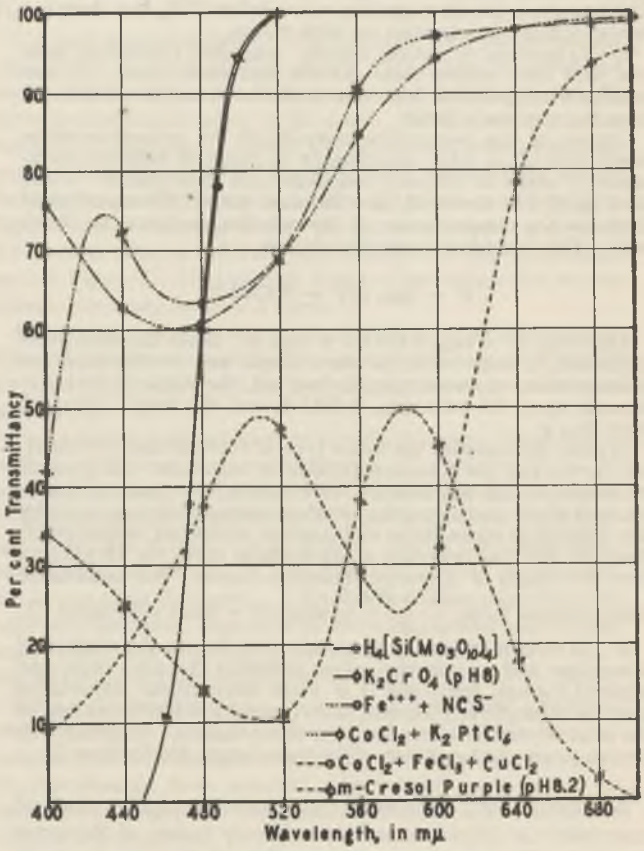

Figure 4. Visually Matched Pairs of Solutions

Study of Colorimetric Standards. In certain analytical methods, such as the comparimetric determination of residual chlorine in drinking water, the nature of the colored system is such that matching with a similarly prepared known solution is impractical. So-called permanent standards, composed of other substances, usually glass disks or aqueous solutions, are used. They are designed to be visually equivalent to the unknown. If spectrophotometrically equivalent (have the same curves), they will match under any kind of illumination. If not, one could have difficulty. Two systems may appear visually identical, under

given illumination, and yet show very different curves (*44*). Figure 4 shows the curves for three pairs of "matching" solutions. A study of such systems led to the interpretation of certain difficulties with the *o*-tolidine method for chlorine (*17*). Incidentally, the chlorine–*o*-tolidine yellow solutions have a band at 436 mμ, but the best visual matching solutions do not. This difference in absorptive capacity of the two systems in the deep blue is not serious for matching, presumably because of the low sensitivity of the eye in this region.

Selection of Filters. A daily problem for many analysts is the selection of filters for the filter photometers which now find extensive use in the colorimetric determination of constituents in a wide variety of materials in many industrial and clinical laboratories. The best basis for such selection is the spectral transmittance curves of the system to be measured and of the available filters. To achieve maximum sensitivity in the photometer, the usual advice is to use a filter whose maximum transmittance is close to the wave length of the peak of the absorption band of the unknown. Figure 5 shows curves for the 1,10-phenanthroline–iron complex and for two glass filters. The wide line centering near 508 mμ is drawn to scale to show the setting of a system to pass a spectral band having 5 mμ width at the peak of the absorption band.

Occasionally, if the curves for filters and constituents are suitably related, it is possible to work with more than one colored substance in solution. An example has been discussed by Knudson, Meloche, and Juday (*36*). Usually colored color-forming reagents are undesirable because any excess added increases the total color, as in the determination of iron with nitroso-R-salt. Inspection of the curves for this reagent and for the iron complex shows the possibility of filtering out the former's color.

Control of Variable Factors. Probably few chemists fully appreciate the importance of color in connection with chemical products and processes. Surprisingly often the production, or avoidance, of given products, or the control of production and operational processes, is based upon color phenomena. In analytical chemistry especially, one or more of at least the following factors are often very important: stability of the color, pH change, temperature, time of reaction, best color-forming reagent, amount of reactant required, order of mixing reactants, state of oxidation, nature of solvent, and interfering ions. Studies of this kind in the author's laboratory (*19, 35, 56, 76, 77, 88, 90*) aimed to study the factors affecting various colors and their formation, and then to establish a set of working conditions that would yield desired analytical results.

In terms of the ultimate effects upon the spectral transmittance curves, two kinds of results may be recognized. One is a change of hue, which is indicated by a horizontal shift of a curve or by a change in its form (to avoid the concentration form-change, one may plot log E as ordinates). Such shifts of position, or real change in the band, mean a change in the nature of the composition of the absorbing medium. It may lead to identification of constituents, as already mentioned. Diverse, colored ions generally change a hue, as do acidity changes in systems subject to pH action. Occasionally a system, such as aqueous cobaltous chloride, is rather sensitive to changes in temperature or the nature of the solvent.

The second kind of result is a change in intensity (luminance), accompanied, of course, by a change in colorimetric purity. This is shown by a change in the height of the peak of the absorption band. Any action decreasing the absorption process is made evident by fading and accompanies a decrease in the absorption band. Examples are diverse ions reacting with the color-forming reactant to give a colorless component or to complex the desired constituent to prevent its functioning. Increase in the band means enhancement of the absorptive capacity by some reaction that must be controlled or prevented.

All these cases necessitate the establishment of some set of conditions to obtain standard reference or working curves. Assuming the applicability of Beer's law, we have a basis for measuring the magnitude of the intensity effects in terms of the desired constituent (*19, 77*). If the effect so calculated does not exceed 2%, it is generally disregarded in the author's laboratory, because so much colorimetric work is not within this limit of accuracy.

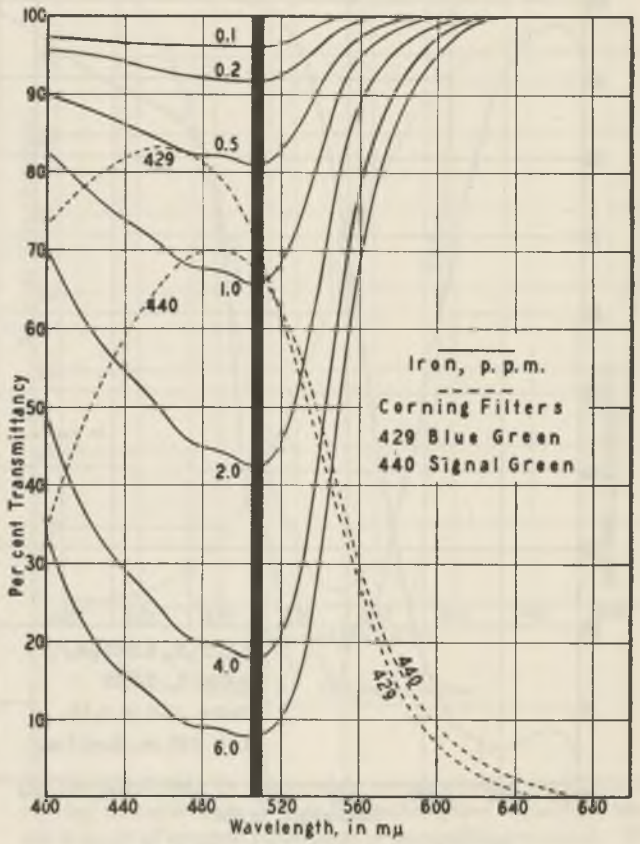

Figure 5. Curves for 1,10-Phenanthroline–Iron Complex and Filters

Finally, for a variety of materials there may be established, in terms of curves, standard specifications of quality and performance. Being permanent, these curves serve for the comparison of subsequent products. In a paint or dye laboratory, for example, data are secured for the standard or desired grades of the materials. Then the effects of processing, impurities, and other measurable factors can be determined in terms of the standard curves. This may lead to change and control of the manufacturing process to achieve permissible color tolerance in the products. Two examples of such uses are for paint (*21, 34*) and for dyes and textiles (*13, 18, 51, 57, 58, 68*).

Provision of General Information. Occasionally curves serve chiefly to satisfy one's curiosity about the nature of a given colored system. Thus, years of use of "modified" pH indicators led to a study of the color transformations in selected solutions (*20*).

Quantitative Uses. Quantitative uses of light absorption spectrometry depend upon the fact that the magnitude of absorption is a function of the concentration of the absorber, which in liquid systems is the solute. The measurements provide the basis for securing a variety of quantitative information (*4, 81, 91*), representative types of which are summarized here.

In the analytical determinations it is customary to make the measurement at the wave length of the peak of the absorption band, although this point is not always the best. With unstable systems the optimum spectral zone may not be that of maxi-

mum absorption (*74*). With more than one colored constituent present, it may be necessary to measure one component on a steep portion of a curve to avoid interference by the second component (*71*). Finally, when simultaneous equations are involved in the calculation, readings are necessary at several points (*10*).

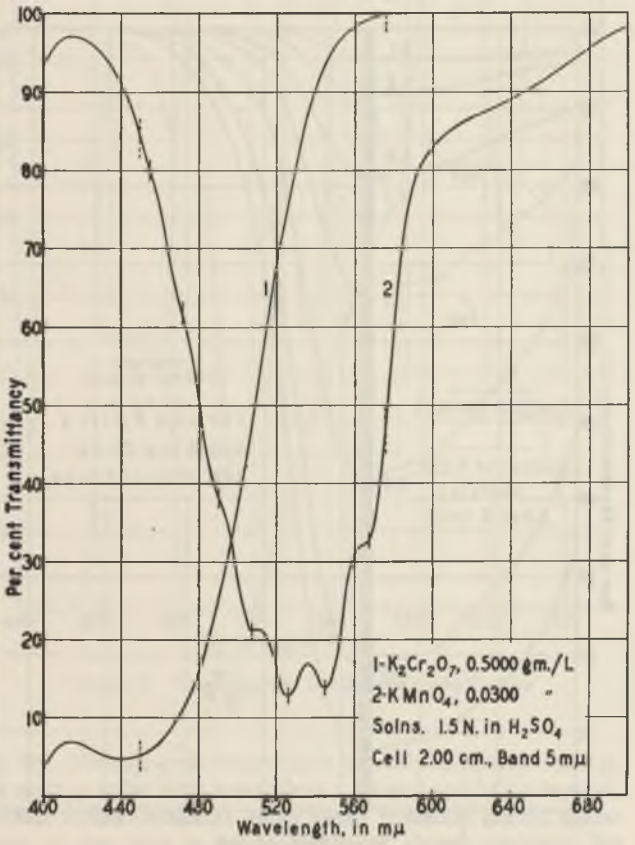

Figure 6. Partially Interfering Binary System

Sensitivity and Range of Method. A set of curves for a series of solutions of suitable concentrations shows, for the specified thickness, the sensitivity of a method of analysis and the range of concentration to which it may be applied reliably without diluting or concentrating the sample. If desired, data for one thickness may be calculated to those for another on the basis of Bouguer's law.

The curves for Figure 5 show the possibilities for a better than average colorimetric method. Some methods are more sensitive, but most of them are not the equal of this one.

As pointed out in Study of Colorimetric Standards and Color Analyses, such curves are fundamental for the sound selection of filters, and for the calculation of I.C.I. numerical specifications.

Conformity of Solutions to Beer's Law. The set of curves described in the preceding section will serve to test a given system for conformity to Beer's law. First the transmittancies or the extinctions for the various concentrations are noted at the wave length of maximum absorption, or as near this point as feasible, if it lies outside the visible range. Then one usually plots as abscissas the concentrations, and as ordinates the extinction or the logarithm of the transmittancy, on a linear scale, or the transmittancy on a logarithmic scale. Straight lines show conformity, a fact which ordinarily needs merely to be stated in a paper. If such a curve is to be used for calculations based on the additive nature of extinction values (*10*), the data should be determined for the instrument used.

Nonconformity to Beer's law indicates the desirability of making comparimetric measurements with a constant-depth standard series method, rather than with a variable-depth instrument. Such deviation may be valuable qualitative evidence of some action affecting the absorber, such as association, dissociation, or ionization.

Analytical Determinations. Although the use of absorptance measurements as a means of making quantitative determinations of desired constituents goes back to the time of Vierordt (*82*), only recently has the availability of instruments made this kind of method fairly well known. The process depends, of course, on relating the absorptive capacity of the solution to the concentration of the desired constituent. Several examples of applying such information will illustrate the possibilities.

For single, colored constituents there are two general procedures. One may work from a calibration curve coordinating concentration and transmittancy (or extinction) determined for a series of solutions of known concentrations. Having determined the transmittancy (or extinction) for an unknown solution, its concentration may be read from the calibration curve. Although a straight-line curve may most nearly satisfy some operators' esthetic sense, such a relationship obviously is unnecessary. Mehlig determined manganese in steel in this way (*41*), and presumably such a method is applicable to any system stable enough for measurement. Usually such procedures are ultimately routinized on filter photometers, since all but the cheapest spectrophotometers are too expensive for wide use.

If the system conforms to Beer's law, the unknown concentration, c, may be calculated from the relationship

$$c = \frac{\log 1/T}{\epsilon b}$$

in which T = the measured transmittancy ($\log 1/T = E$ = extinction), ϵ = the molecular extinction, and b = the thickness. One must have determined ϵ at thickness b. Using this method, Mehlig's results on copper in ores and mattes (*42*) were as reliable as the best titrimetric determinations and somewhat more rapid. Later he applied the same technique to determining iron in ores (*43*).

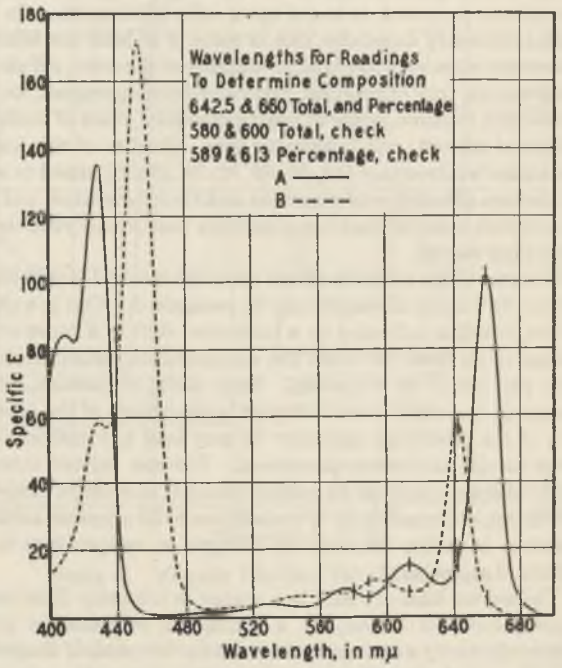

Figure 7. Pure Chlorophylls A and B

Incidentally, the values for copper ranged from 2 to 21%, and those for iron from 36 to 57%. This is noteworthy in view of the very general belief that colorimetric determinations are limited to maximum concentrations of a few parts per million of desired constituent. Even more surprising is the range of concentration covered in work by Drabkin, *et al.* (*16*). The upper limit for reliable work with modern instruments needs further study for representative systems.

With two colored constituents present, several situations may be encountered. The curves for the two may be so similar that spectrometric determination is not feasible. Many yellow solutions, for example, are closely related in their light absorptive capacity. It may be possible to avoid the effect of one constituent by oxidation or reduction, complexation, or other kind of chemical reaction (*4*).

If the two curves are suitably related, either or both constituents may be determinable. The possibilities may be illustrated by examples from recent papers. Silverthorn and Curtis (*71*) determined manganese and chromium simultaneously in steel. Figure 6 shows the transmittancy curves for one concentration of dichromate and of permanganate, as determined on a recording instrument operating on a spectral band width of 5 mμ. Silverthorn and Curtis recommend reading transmittancies at 450 and 575 mμ. They assume no absorption by dichromate at the upper wave length. This reading provides then for measuring the manganese, as outlined above. At 450 mμ both dichromate and permanganate absorb. Knowing the amount of manganese from the reading at 575 mμ, its absorption at 450 mμ may be subtracted from the total absorption. The difference, resulting from the dichromate, enables one to calculate the chromium. Since logarithmic values enter the calculations, the systems should conform to Beer's law.

In the most complicated case, where neither constituent can be isolated spectrally, the measurement is made upon the mixed components at carefully selected wave lengths. Using these data, together with values of the absorptive capacity at these same wave lengths for each pure constituent, it is possible to calculate the amount of the separate components by means of simultaneous equations. Because of the nature of the calculations, it is of great importance to have the absorptive values determined as reliably as possible. In any case, the curves for the two components must be suitably related, as pointed out by Comar and Zscheile (*10*). With superb experimental facilities and technique, they have shown what can be done analytically on a mixture of the two closely related chlorophylls. The curves for the two pure compounds are shown in Figure 7, with the wave lengths marked at which readings are made.

In addition to using this kind of method for such binary systems, Miller (*49*) has extended it to ternary and quaternary systems. Such procedures are the finest examples of the quantitative analytical application of spectrophotometers. To what other method of measurement could one turn?

Table I. Colorimetric Analyses

		Trichromatic Values[a]		
		Red	Green	Blue
		%	%	%
Glasses	Blue	17.3	7.7	75.0
	Yellow	50.0	45.7	4.3
	Red	68.9	31.1	0.0
Flag[b]	Red	56	32	12
	White	32	33	35
	Blue	28	26	46

		Monochromatic Values		
		Dominant wave length	Luminance	Purity
		mμ	%	%
Glasses	Blue	460	6.1	83
	Yellow	582	41.6	89
	Red	619	14.6	100

[a] Actually, one calculates, and the flag of the United States is specified in, the decimal chromaticity coordinates, x and y. Then $z = 1 - (x + y)$. Multiplying each trichromatic coefficient by 100 gives the respective percentages shown for red, green, and blue.
[b] Federal Specification TT-C-591 (1934).

Perhaps a word of caution should be directed to the novice in spectrophotometry. With the best of modern instruments, a competent operator can determine absorptance data satisfactorily. The question is whether the system was prepared so that the measurement was worth making. Morton (*54*) has summarized the formidable difficulties encountered in applying the absorptometric method to vitamin A in the ultraviolet. Similar problems arise in colorimetry. Elsewhere the author has outlined some of these chemical problems (*48*).

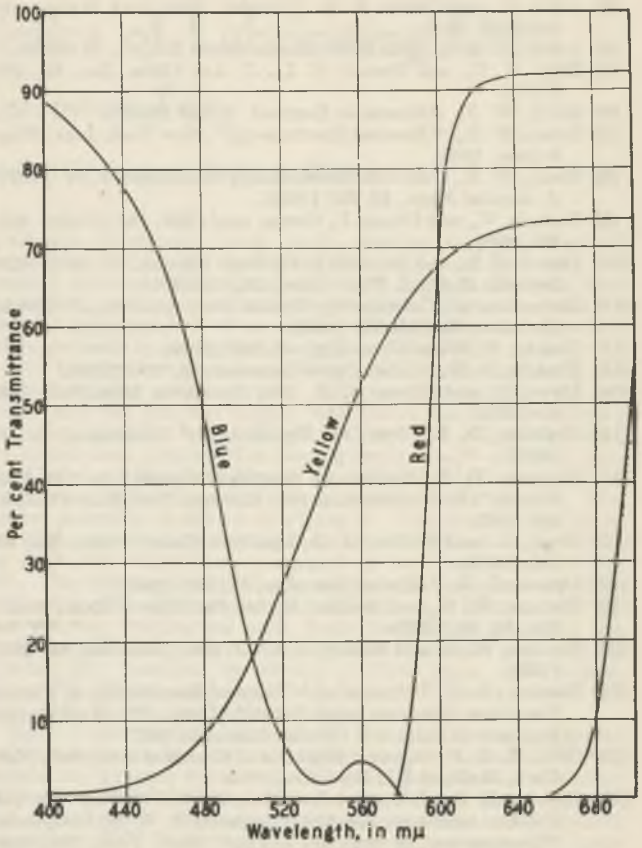

Figure 8. Standard Glasses

Color Analysis. In colorimetric specification of materials, involving measurement of their light absorptive capacities, most use is made of spectral reflectance or transmittance curves. The data may be considered as objective, especially when determined with a high quality photoelectric instrument.

The curves may be adequate as such. Thus, the transmittance curves in Figure 8 show the general colorimetric characteristics of the three standard glasses used in the author's laboratory for photometric checking. If desired, the numerical specifications of the color may be calculated in terms of trichromatic and/or monochromatic values (*79*). Hardy's handbook which incorporates the 1931 I.C.I. recommendations, is the standard reference work for calculating numerical specifications from spectrophotometric curves in terms of the standard illuminants *A*, *B*, or *C* (*28*). A calculator (*78*) greatly facilitates the work. Table I gives these numerical values, as computed by the author, for the three glasses whose curves are shown in Figure 8. The values are for illuminant *C*, using 30 selected ordinates. As a matter of interest, there are included the values (converted to percentages) for the U. S. flag, as specified by the Federal Specifications Executive Committee on Color.

Chemical publications thus far contain few such data, but this kind of information is coming into use in general specification work (*2*, *28*, *52*, *60*). Related to this type of application is the suggestion for methods for computing the formulation of colorants needed to effect a visual color match of a given standard from spectrophotometric measurements of the colorants and the standard (*59*).

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[End of Symposium]

Bearing Corrosion Characteristics of Lubricating Oils

Indiana Stirring Corrosion Test

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NUMEROUS laboratory bearing corrosion test methods have been reported in the literature, but are of basic value only in so far as they predict service performance or help explain the nature or mechanism of the bearing corrosion phenomenon. Actual correlation with service is practically impossible to establish, since some very bad (by accelerated tests) oils cause corrosion only in exceptionally severe service, and, infrequently, even very good oils cause corrosion in service under abnormal, but not necessarily severe, conditions. The only practical correlation is that between laboratory tests and standard accelerated engine tests.

The present study is limited to a comparison of laboratory corrosion test results with Chevrolet 36-hour test results. Of interest comparable to the correlation established between the laboratory and Chevrolet tests is the demonstration of the enormous effect, specific to certain oils, of the several catalysts used.

Table I. Laboratory Bearing Corrosion Test Methods

Stirring Tests	Air Blowing Tests	Circulating Oil Test
Caterpillar corrosion test[a]	Continental test (*14*)	Underwood test (*11*)
Indiana stirring test (*4*)	Sohio test (*1*)	
MacCoull test (*8*)	Shell existent corrosion test (*12*)	
Shell thrust corrosion test (*10*)		
Shell corrosion and stability test (*13*)		

[a] This is not a "stirring" test in the same sense as the other four tests. Instead of rapid stirring, it provides for stirring at 60 r.p.m., sufficient to keep the oil circulating.

The various laboratory bearing corrosion tests are characterized by the type of apparatus used and the test conditions selected. Based on type of apparatus, the more prominent tests may be classified roughly into three groups as shown in Table I.

The merit of rapid stirring, providing thorough and intimate mixing of air and oil, has been recognized in four of these stirring tests. Moreover, there are other miscellaneous advantages in this type of test. It is readily adapted to being run in the multiunit type of apparatus, the parts are readily removed and easily cleaned, and it is suitable for uniformly suspending powdered catalysts.

In this work, a modification of the Indiana stirring oxidation test has been used. No special merit is claimed for this method over the other stirring-type tests, except perhaps in simplicity. It would be desirable if, from the variety of stirring-type tests available, one test would ultimately emerge, incorporating the best, but only the essential, features of each method. The present study is concerned not so much with the test method as with the conditions under which the test is run, particularly as regards catalysts used. Some attention is also given to the nature of the bearing metal test strips used.

INDIANA STIRRING CORROSION TEST METHOD

APPARATUS. The apparatus used for the test is essentially the same as the original Indiana stirring oxidation test apparatus (*4*). The mechanical setup has been improved considerably, a multiunit aluminum block bath, similar to the MacCoull apparatus, being used instead of the original oil bath unit. A smaller, more versatile, aluminum block unit has also been used for varying stirring speed and temperature. Figure 1 shows the general appearance of these units. The smaller bath provides stirring speeds in convenient steps from 100 to 5000 r.p.m.

The test beaker used is a 500-cc. tall-form beaker as in the original stirring oxidation test. However, no varnish rods are used; and the iron and copper catalysts of the Indiana stirring oxidation test have been replaced by 3 × 1 cm. strips of (*a*) lead, (*b*) copper-lead, bearing (flat bearing stock, Cu-Pb on steel, from the Cleveland Graphite Bronze Co., Cleveland, Ohio), and (*c*) copper, suspended from a three-pronged, iron wire support. The beaker assembly is shown in Figure 2. The metal strips serve the dual purpose of catalyzing the oil oxidation and of providing, by their own weight loss, a measure of the corrosiveness of the oil. The wire support holds the strips with one side very close to the side of the beaker when the oil is at rest. However, during the test the swirling oil pulls them toward the center of the beaker, so that all parts of the strips are in contact with rapidly moving oil. Aeration by stirring at 1300 r.p.m. with a glass stirrer (two blades, rounded, 2 × 2 cm., at 40° pitch) remains the same as in the original Indiana stirring oxidation test.

TEST CONDITIONS. Although the Indiana stirring corrosion test has been studied over a range of temperatures and stirring speeds, the present work is almost entirely limited to operation of the test at 300° F. and 1300 r.p.m. It was found early in the investigation that, when the temperature was increased much over 300° F., some oils that showed low corrosion losses in the Chevrolet 36-hour test were highly corrosive in the laboratory test. For this reason it has been considered more significant to accelerate corrosion by the addition of catalysts than by abnormal temperature conditions; 1300 r.p.m. represents a compromise between the desirable feature of more rapid oxidation (and corrosion) at higher stirring speeds and the impracticability of the higher stirring speeds due to splashing of the oil in the open beaker used.

The standard test conditions for the Indiana stirring corrosion test in the present study are summarized in Table II.

Test results are generally expressed as hours elapsed until 33 mg. per sq. cm. of lead corrosion occurs. It is believed that

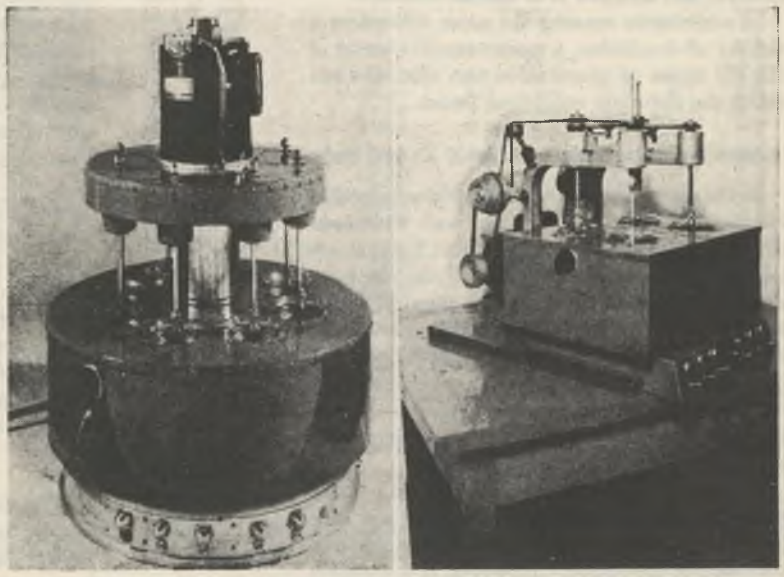

Figure 1. Indiana Stirring Corrosion Test Apparatus
Aluminum blocks and stirring rigs

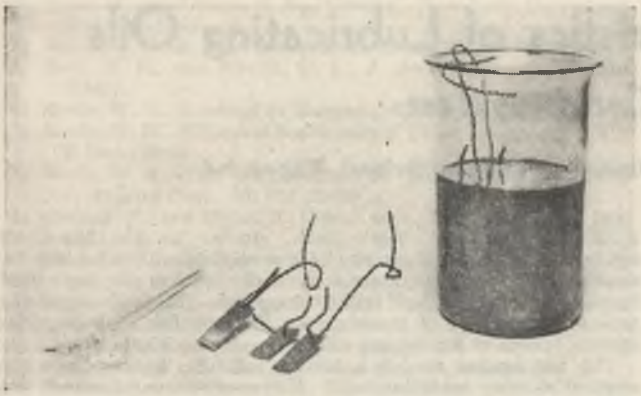

Figure 2. Indiana Stirring Corrosion Test Apparatus
Beaker, test strips, and stirrer

results expressed in this way are of much more significance than results expressed as amount of corrosion at a given time, because of the autocatalytic nature of lead corrosion in most of the tests. An unfortunate choice of a definite time duration for the test might well show one oil ten times as good as another, whereas the true comparison would show perhaps a 10% difference (for shape of time-corrosion curves, see Figure 3). The time for 33 mg. of lead loss per sq. cm. of surface was chosen as a criterion because at this time the induction period is definitely over and the period of rapid corrosion has been reached (if such autocatalytic behavior is characteristic of the oil being tested).

Although the copper-lead and copper strips were weighed periodically just as were the lead strips, no results are reported on the corrosion of these strips. In almost all cases their losses were negligible.

Table II. ISC Test Conditions

Sample, 250 cc. of oil in a 500-cc. tall-form beaker
Temperature, 300° F.
Aeration, stirring at 1300 r.p.m. with a glass stirrer (two blades, rounded, 2 × 2 cm., at a 40° pitch)
Catalyst, 3 × 1 cm. strips of Pb, Cu-Pb, Cu, plus various powdered catalysts
Test strips, identical with metal catalyst strips
Duration, 100 hours, or until the lead strip has lost 33 mg. per sq. cm. of surface

Table III. Oils Used in Indiana Stirring Corrosion Tests

Designation	Description	Chevrolet 36-Hour Test Results[a], Grams of Cu-Pb Loss per Whole Bearing
Oil 1	A solvent-extracted M.C. 30 grade oil + a detergent type, phosphorus-containing additive (blended oil, 0.042% P)	1.9
Oil 2	No. 1 plus an aromatic amine inhibitor	0.5
Oil 3	No. 1 plus a sulfurized hydrocarbon (blended oil, 0.075% added S)	0.2–1.3[b]
Oil 4	No. 1 plus a sulfurized hydrocarbon (blended oil, 0.15% added S)	0.2
Oil 5	Commercially available H.D. oil, extremely stable toward bearing corrosion	0.1
B-1	Cooperative test oil	0.7
B-3	Cooperative test oil	0.5

[a] Indiana results on all oils are shown. In every case, a number of closely checking values have been obtained or results have been duplicated in other laboratories. Results on B-1 and B-3 are very close to averages of cooperative test results (*9*).
[b] In the Chevrolet test this oil shows an induction period followed by a rapid increase in corrosion rate. Depending on inherent variations in severity of test, induction period may end before or after 36 hours.

TEST OILS USED

The seven oils chosen for the investigation of the effect of different catalysts are described in Table III, with Chevrolet 36-hour test results on these oils. The seven oils represent a wide variety of additives and give Chevrolet test corrosion results ranging from very poor to very good. The present study was limited to additive-containing oils, since the relation between catalyst and additive is of special interest.

In addition to running the seven oils under a variety of conditions, a more extensive series of oils (D series of cooperative test oils) was run under the optimum conditions found.

SIGNIFICANCE OF CHOICE OF LEAD AS TEST STRIP

In the variety of bearing corrosion tests available, lead, copper-lead, copper, and cadmium-silver test strips have all been used for evaluating the corrosive tendencies of oils—in most cases meaning their corrosiveness toward copper-lead bearings. It is the authors' experience that in a test where the bearings are not rubbed, the corrosion of lead strips is of more significance with respect to the corrosion of copper-lead bearings in the engine than is the corrosion of copper-lead, copper, or cadmium-silver strips.

Copper-lead bearing strips, offhand, would seem the most logical test strips for use in a laboratory test to predict copper-lead bearing corrosion in the engine. However, it is common experience that it is extremely difficult to cause extensive copper-lead corrosion in laboratory tests unless a high temperature—e.g., in the neighborhood of 350° F.—or severe rubbing of the strips is one of the test conditions.

Copper strips show appreciable weight losses only when special conditions exist, such as when the oil is oxidizing extremely rap-

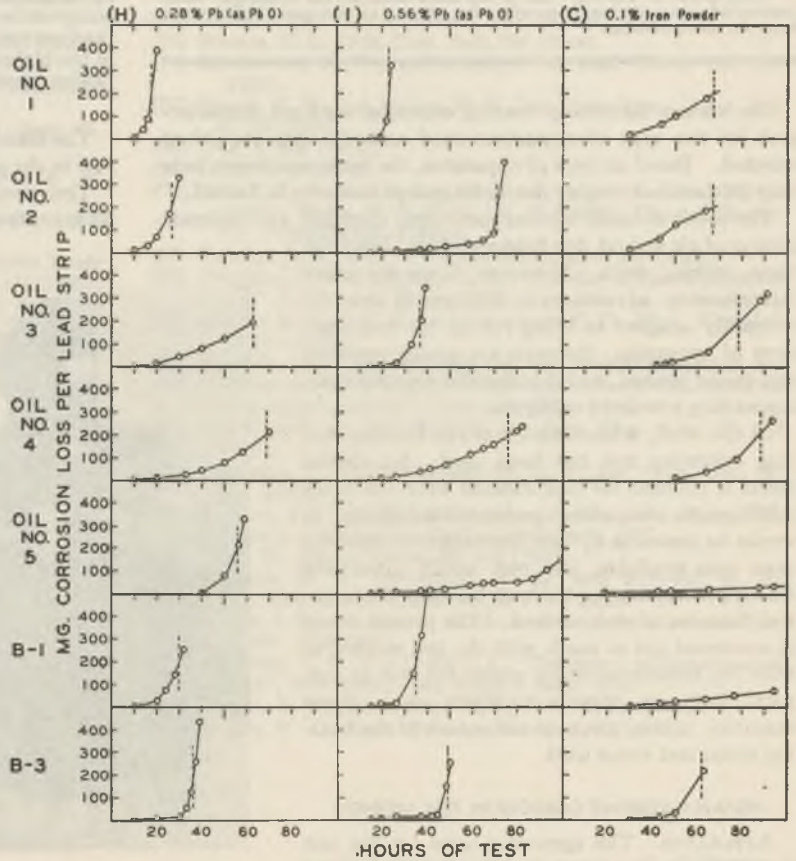

Figure 3. Indiana Stirring Corrosion Tests
Time-corrosion curves

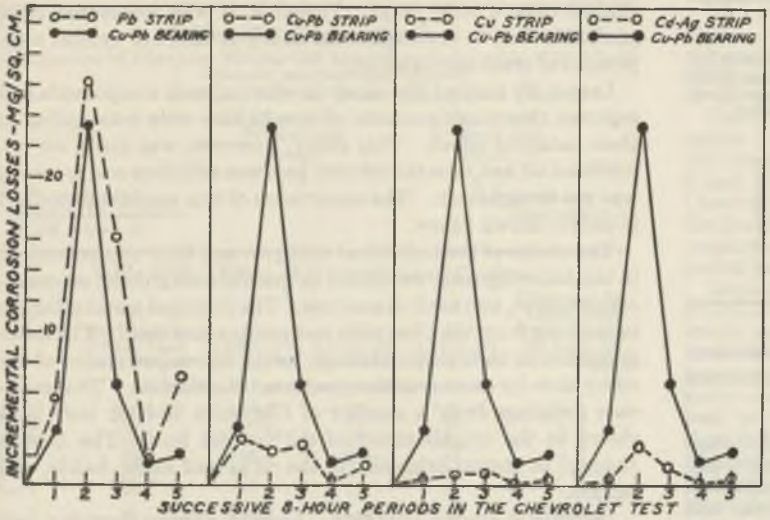

Figure 4. Comparison of Strip Losses with Copper-Lead Bearing Losses
Chevrolet 36-hour test, oil 1

idly, and usually then only at high temperatures; when the oil contains very active sulfur, and, again, high temperatures exist, and at low temperatures in the presence of water (in the liquid phase). None of these conditions are representative of the corrosion that ordinarily occurs in the Chevrolet 36-hour test.

Cadmium-silver bearings corrode rapidly when the oil reaches the stage of rapid oxidation. Results on cadmium-silver corrosion do not reflect any of the specific corrosive effects some additives show toward copper-lead bearings. Moreover, Livingston (*7*) and Waters (*12*) have shown that cadmium-silver bearings respond entirely differently than copper-lead bearings to corrosive oils over the temperature range of 200° to 300° F.

Lead strip corrosion in laboratory tests is due either to oil oxidation or to the specific effect of additives. It is generally believed that almost invariably copper-lead corrosion in the engine is due to selective removal of lead. Larsen (*5*) has shown how thin platings of lead may be used for determining whether an oil, "as is", is corrosive. Lead sometimes forms protective films in laboratory tests which may make the oil appear unduly stable, but it is less subject to such film formation than are the other types of test strips.

As evidence that lead strips are most suitable for use in laboratory tests, where no mechanical rubbing of the bearing occurs, the following tests are cited. Four oils were run in the Chevrolet 36-hour test with small strips (3 × 1 cm.) of each of the four bearing metals wired in the crankcase. The bearing weight losses and the strip losses were obtained periodically. Results are summarized in Table IV and in Figure 4. Generally only the lead strips showed appreciable losses and these losses reasonably paralleled those of the copper-lead bearing.

It is realized that the above data were obtained with a limited number of oils and might not represent an accurate picture if a wider variety of oils were included. As far as it goes, it is very strong evidence that lead test specimens should be used in a laboratory test where the bearing is not mechanically rubbed. Thus, if it is possible to oxidize the oil in a laboratory test corresponding to the way it oxidizes in the engine, the lead losses in the laboratory test will predict copper-lead bearing losses in the engine.

EFFECT OF SOLID CATALYSTS

In the majority of the bearing corrosion tests described in the literature, no catalysts other than metal surfaces are used. Some work has been done with metal naphthenates as catalysts, but results have been inconclusive. In the light of the recent work reported by Larsen (*6*), showing the enormous catalytic effect of the suspended solids in crankcase drainings, it has seemed logical to examine carefully the effect of crankcase catalyst and its probable constituents on bearing corrosion.

Practically all the metal catalysts present in engine tests are originally present in solid form. These catalysts become soluble in the oil as a result of their reaction with oxidized oil or with additives in the oil. Generally, the oil-soluble compounds of the metals mole for mole, are much more active catalytically than the originally occurring insoluble form. A large part of the oxidation (and corrosion) inhibiting properties of a particular oil may reside in the oil's effectiveness in preventing the solid catalysts from changing to an oil-soluble form. Davis (*2*) reported that the extent of bearing corrosion in engine tests correlates reasonably well with the oil-soluble lead content of the used oil, showing that the oils which protected the bearings from corrosion likewise prevented the formation of high concentration of oil-soluble lead salts.

Early in the present study, tests were run using iron and lead naphthenates as catalysts. It was noted in the case of one oil that the corrosion rate with 0.01% iron (added to the oil as iron naphthenate) was just about 3 times as rapid as with 0.01% lead (added to the oil as lead naphthenate). This difference corresponded to the amounts of the naphthenates actually used, since the iron naphthenate analyzed 10% iron and the lead naphthenate 30% lead. This suggested that the acid radical instead of the metal was controlling the corrosion rate. Tests using free naphthenic acids showed this to be the case and that the corrosion rate was almost directly proportional to the concentration of naphthenic acid. These results were obtained on only one type of oil but are sufficient to show that metal naphthenates are not suitable catalysts for all oils.

For the above reasons, attention has been centered on solid catalysts in the present work rather than on oil-soluble catalysts. The specific effect of some of these catalysts on certain oils is amazing.

Table IV. (Extended) Chevrolet 36-Hour Tests

(Comparison of metal strip corrosion losses with Cu-Pb bearing corrosion losses)

Oil	Period of Test	Cu-Pb bearing	Corrosion Loss — Test Strips			
			Pb	Cu-Pb	Cu	Cd-Ag
	Hours		*Mg./sq. cm. of surface*			
No. 3	0–8	1.6	(5.7)[a]	0.4	0.0	0.3
	8–16	0.7		0.0	0.0	0.2
	10–32	2.7	2.0	0.1	0.1	0.3
	32–36	3.0	4.5	0.2	0.1	0.3
	36–44	3.9	6.0	0.0	0.0	0.2
B-1	0– 8	1.4	1.2	0.3	0.0	0.5
	8–16	2.7	4.1	0.2	0.0	0.1
	16–24	2.9	5.8	0.6	0.1	0.2
	24–32	1.6	[b]	1.8	0.0	0.5
	32–36	0.5	[b]	0.9	0.1	0.2
Similar to No. 1, but S.A.E. 20 grade	0–10	20.0	33	5.0	0.7	...
	10–20	2.9	30	6.3	0.7	...
	20–30	4.1	12	1.6	0.5	...
	30–40	2.5	8	3.3	1.3	...
	40–50	3.2	11	3.0	0.3	...
	50–60	2.7	11	2.6	1.3	...

[a] Weight not taken at 8 hours; 5.7 mg. is weight loss 0 to 16 hours.
[b] Pb strip out, mechanically battered.

CRANKCASE CATALYSTS. Offhand, it would seem that crankcase catalyst would be ideal for laboratory tests. However, it cannot be isolated as it originally occurs in the engine, but is obtained after alteration to some unknown extent by reaction with the oil during running in the engine. This may not be a serious objection, but in any case it would be preferable to use a catalyst of definite chemical composition, containing only those

Table V. Effect of Crankcase Catalyst

Oil	A No Catalyst (Other than Test Strips)	B 0.5% Crankcase Catalyst	Chevrolet 36-Hour Test, Grams of Cu-Pb Loss per Whole Bearing
	Hours for 33 mg. per sq. cm. Pb loss		
No. 5	100+	100+	0.1
No. 4	83	100+	0.2
No. 2	52	14	0.5
B-3	78	32	0.5
B-1	100+	16	0.7
No. 1	62	19	1.9
No. 3	81	80	0.2–1.3

constituents which have a major catalytic effect on corrosion. Preceding work of this kind, tests were first made using crankcase catalyst.

Crankcase catalyst was separated from the crankcase drainings from a Chevrolet 36-hour test on uninhibited, solvent-extracted, M.C. 30 grade oil by centrifuging and washing the precipitated solids with hexane. It contained approximately 45% lead and 2% iron.

Indiana stirring corrosion tests were made on the seven test oils containing 0.5% of the above catalyst. Results are shown in Table V, along with results obtained using no catalyst other than the metal test strips. In this and subsequent tables on the effect of different catalysts, the oils are arranged in order of increasing corrosion in the Chevrolet 36-hour test. Oil 3, giving variable results in the Chevrolet test, has no definite place in the series and is listed at the bottom of the table. For perfect correlation with the Chevrolet test, the Indiana stirring corrosion test results should be highest for the first oil in the series and should show decreasing values going from the top to the bottom of the table.

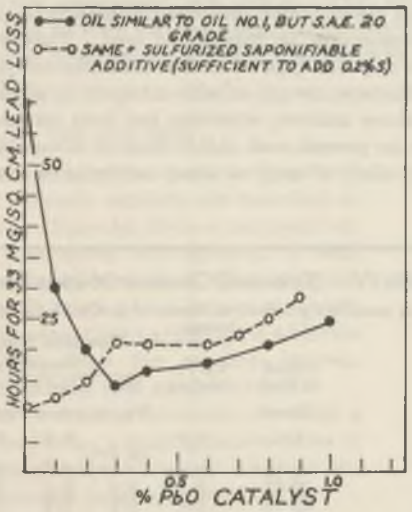

Figure 5. Effect of Concentration of Lead Oxide on a Detergent Oil with and without Sulfurized Saponifiable Additive

Comparing the A and B series of results, it is evident that 0.5% crankcase catalyst accelerated corrosion in the case of oils 1, 2, B-1, and B-3. It did not effect No. 3 (containing the lower concentration of sulfurized hydrocarbon) and actually stabilized No. 4 (containing the higher concentration of sulfurized hydrocarbon). Oil 5 was too stable in both tests to make comparisons. Evidently the sulfurized hydrocarbon is a more effective deactivator of crankcase catalyst than the aromatic amine (oil 2) or the inhibitors in B-1 and B-3.

Obviously the test using 0.5% crankcase catalyst does not line up satisfactorily with Chevrolet 36-hour tests. This indicates that the use of 0.5% crankcase catalyst does not present a complete picture of the catalytic activity in Chevrolet tests. It is entirely possible that better correlation would be obtained if the concentration of crankcase catalyst and the temperature were studied over a wide range. However, it was considered more profitable first to investigate the catalytic effect of typical components of crankcase catalyst.

Larsen (*6*) studied the catalytic effect of such components and reported that small amounts of iron halides were outstanding in their catalytic effect. This study, however, was made on uninhibited oil and thus the relation between additives and catalysts was not brought out. The importance of this combination effect is clearly shown below.

The choice of the individual catalysts and their concentrations in the following tests was based on general background, on crankcase catalyst, and used oil analyses. The principal metal catalysts in used oils from the Chevrolet test are iron and lead. The latter is present in high concentrations, owing to contamination of the oil by blow-by decomposition products from the fuel. The crankcase drainings from a number of Chevrolet 36-hour tests have shown in the neighborhood of 0.5% total lead. The lead is thought to appear originally in the oil as lead oxide, halide, and sulfate.

Inorganic Iron Catalysts. Indiana stirring corrosion test results in the presence of two concentrations of reduced iron powder, and two concentrations of ferric chloride are summarized in Table VI.

The iron powder has no effect or a slightly beneficial effect with all oils except B-3, in which case it has a mild catalytic effect. Obviously, the use of iron powder in the Indiana stirring corrosion tests is no improvement as far as correlation with the Chevrolet tests is concerned.

The lower concentration of ferric chloride (series E) has a pronounced catalytic effect on B-1 and B-3, a somewhat lesser effect on oils 1 and 2, and no effect on oil 5 nor on the two oils containing sulfurized hydrocarbon. Increasing the concentration of ferric chloride tenfold lowers the stability of the three oils previously not affected, and increases the stability of the other oils (excepting oil 2). Neither the E nor F series of results comes close to satisfactory correlation with the Chevrolet test results. It is extremely doubtful if the concentration of active iron catalyst ever approaches the 0.1% concentration used in series F.

The positive catalytic effect of ferric chloride in most of the above tests qualitatively checks Larsen's results (*6*), but the effect of ferric chloride on additive-containing oils is not nearly so great as he found for uninhibited oils. The unexpected, increased stability observed with oils B-1 and B-3 when the ferric chloride concentration was increased tenfold demonstrates the complexity of the corrosion phenomenon and emphasizes the caution that must be exercised in interpreting any one set of test results.

Inorganic Lead Catalysts. Previous to the present study, a number of tests had been made, using powdered lead oxide as catalyst. This work was suggested by the seemingly anomalous results obtained with two oils in the Chevrolet 36-hour test and in the G.M. Diesel 500-hour test. These results are shown in Table VII.

Thus the addition of the sulfur-saponifiable additive to oil 1 greatly improves the Chevrolet performance but accelerates corrosion in the Diesel test. These data, incidentally, illustrate the futility of trying to develop a single laboratory test for pre-

Table VI. Effect of Inorganic Iron Catalysts

Oil	A No Catalyst (Other than Test Strips)	C 0.1% Fe Powder	D 1.0% Fe Powder	E 0.01% Fe (as $FeCl_3$)	F 0.10% Fe (as $FeCl_3$)	Chevrolet 36-Hour Test, Grams of Cu-Pb Loss per Whole Bearing
	Hours for 33 mg. per sq. cm. Pb loss					
No. 5	100+	100+	100+	100+	86	0.1
No. 4	83	88	100+	100+	54	0.2
No. 2	52	67	67	38	27	0.5
B-3	78	62	55	16	70	0.5
B-1	100+	80+	100+	11	90	0.7
No. 1	62	67	95	37	45	1.9
No. 3	81	78	76	75	41	0.2–1.3

Table VII. Comparative Tests

(Comparison of Chevrolet 36-hour test bearing corrosion with G.M. Diesel 500-hour test bearing corrosion)

Oil	Cu-Pb Loss per Whole Bearing (Rod Bearing) Chevrolet 36-hour test	G.M. Diesel 500-hour test
	Grams	*Gram*
No. 1	1.9	0.1
No. 1 plus sulfur-saponifiable additive (0.2% added S)	0.3	0.6 (48 hours, test discontinued)

Table VIII. Effect of Inorganic Lead Catalysts

Oil	A No Catalyst (Other than Test Strips)	G 0.28% Pb (as $PbCl_2$)	H 0.28% Pb (as PbO)	I 0.56% Pb (as PbO)	Chevrolet 36-Hour Test, Grams of Cu-Pb Loss per Whole Bearing
	Hours for 33 mg. per sq. cm. Pb loss				
No. 5	100+	100+	56	100+	0.1
No. 4	83	100+	79	76	0.2
No. 2	52	50	27	71	0.5
B-3	79	66	36	49	0.5
B-1	100+	91	30	35	0.7
No. 1	62	87	18	23	1.9
No. 3	81	100+	63	37	0.2–1.3

dicting bearing corrosion in more than one type of engine test. Although there is a 50° F. difference between the sump temperatures in the two tests, other considerations indicated that the differences in performance were mainly due to the presence of lead catalysts from the fuel in the Chevrolet test and their absence in the Diesel tests.

Indiana stirring corrosion tests with various concentrations of powdered lead oxide catalyst were run on the two oils. Results are shown graphically in Figure 5. In the absence of lead oxide, oil 1 (S.A.E. 20 grade) is more stable than the oil containing the sulfur compound. This is in accord with the G.M. Diesel results. Increasing the concentration of lead oxide caused a sharp drop in stability up to 0.3% lead oxide, followed by a gradual increase in stability as amounts of lead oxide in excess of 0.3% were used. The addition of increasing amounts of lead oxide to the oil containing the sulfur-saponifiable additive increased the stability gradually over the whole range of lead oxide concentrations. Thus, at concentrations of lead oxide of 0.3% or greater, the oil containing the sulfur compound is more stable. This is qualitatively in accord with the Chevrolet test results.

The minimum stability observed with oil 1 at a concentration of 0.3% lead oxide proved to be of interest. This concentration of lead oxide is just sufficient to neutralize the dibasic acid theoretically possible from 0.042% phosphorus. To check that this behavior was not a coincidence, similar series of tests were run on oils containing (*a*) half the concentration of the additive and (*b*) twice the concentration of the additive (Figure 6). It is evident that in each case a minimum stability was shown at that concentration of lead oxide sufficient to neutralize completely the theoretical dibasic acid from the phosphorus present. Increased amounts of lead oxide had a definite inhibiting effect. Indications of similar behavior have been obtained on oils containing other phosphorus-type additives.

To investigate further the inhibiting effect of lead oxide, oil 1 (S.A.E. 20 grade) was subjected to the Indiana stirring corrosion test (0.3% lead oxide catalyst) until a rapid rate of lead corrosion had been established. Excess lead oxide was added and the test continued. The corrosion of the lead strip stopped immediately on the addition of excess lead oxide (Figure 7).

The above data shed some light on the confusion which has existed concerning the effect of leaded fuel on bearing corrosion, by illustrating how the lead from the fuel can act either as an inhibitor or as an accelerator of corrosion. Such behavior has previously been observed in engine tests (*3*). This dual action is entirely absent when lead naphthenate is used as catalyst; corrosion is either accelerated or not affected, depending upon whether a sufficiently powerful deactivator of oil-soluble lead is present. Indiana stirring corrosion tests on the seven test oils in the presence of lead chloride and in the presence of two concentrations of lead oxide are summarized in Table VIII.

The catalytic effect of 0.28% lead (as lead chloride) is relatively mild. It causes a slight increase in stability in the case of several oils and a slight decrease with others. Use of this catalyst shows little promise of causing the Indiana stirring corrosion test results to correlate with the Chevrolet test results.

The presence of 0.28% lead (as lead oxide) (H series of tests) causes a marked lowering of stability against corrosion for all oils except those containing the sulfurized hydrocarbon (Nos. 3 and 4). The correlation of the H series of results with the Chevrolet results is satisfactory with the following exceptions: the beneficial effect of the aromatic amine in oil 2 is not so pronounced as would be expected from engine tests, and the induction period for oil 5 is somewhat low.

Doubling the concentration of lead (I series of tests), gives very interesting results. Oil 1 shows a slight increase in stability, as would be expected from previous tests. Oil 2 more than doubles in stability, the beneficial effect of the amine inhibitor apparently increasing with increasing concentrations of lead oxide. Oil 3 shows a sharp drop in stability. This is not surprising since the lead concentration has been increased beyond the amount theoretically equivalent to the sulfur (0.075%) present due to the sulfurized hydrocarbon. The marked variation in the stability of oil 3, depending upon the amount of lead used as catalyst, may well be the explanation of the erratic results obtained in the Chevrolet test. Oil 4, containing sufficient sulfur compound to deactivate all the lead, is not affected by the increase in catalyst. Oil 5 shows a marked increase in stability and B-1 and B-3 show slight increases in stability due to the increased concentration of lead oxide.

The correlation of the I series of results with the Chevrolet 36-hour test is promising. Oil 2 is the only oil out of line, showing too high a stability. However, comparison of the H and I series results indicates that, very probably at some intermediate concentration of lead—e.g., 0.46% lead (as lead oxide)—this oil

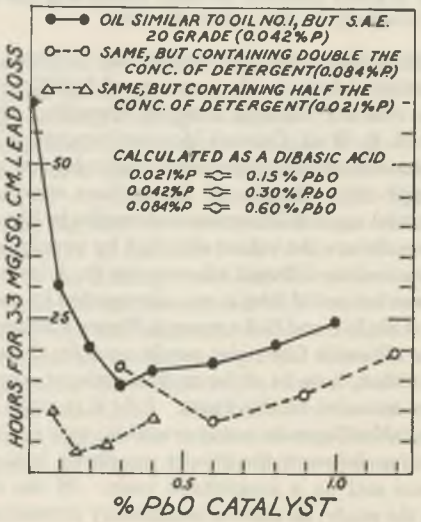

Figure 6. Effect of Concentration of Lead Oxide on Oil Containing Different Amounts of Detergent

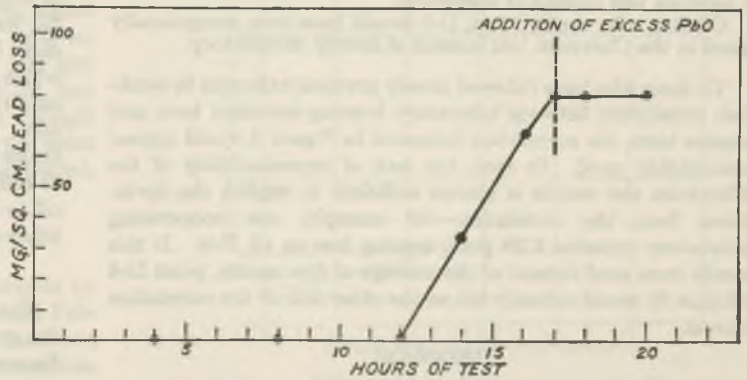

Figure 7. Corrosion-Inhibiting Effect of Excess Lead Oxide Catalyst

Oil similar to No. 1 but S.A.E. 20 grade; catalyst, 0.30% lead oxide (added at start of test)

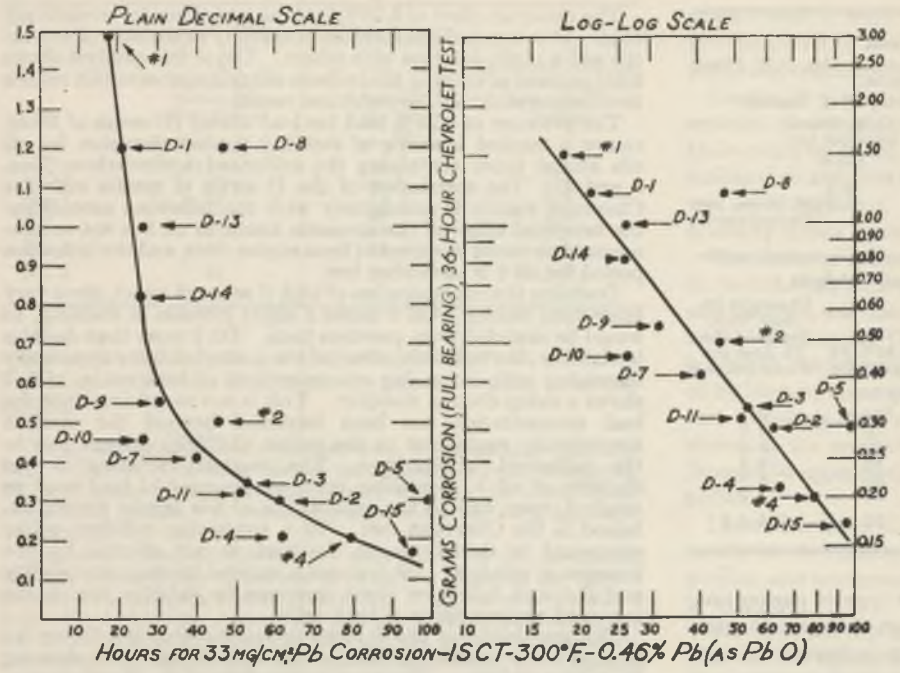

Figure 8. Indiana Stirring Corrosion Test Results Plotted against Chevrolet Test Results

would show a lower stability without disturbing the correlation already satisfactory for the other six oils.

LEAD OXIDE CATALYST, D SERIES OF COOPERATIVE TEST OILS. A series of tests in the presence of 0.46% lead (as lead oxide) was run on thirteen samples (provided through the courtesy of H. R. Wolf, General Motors Corporation) that were available from the recent cooperative Chevrolet test program on detergent-type oils. Results of the Indiana stirring corrosion tests are plotted against Chevrolet test results in Figure 8. The Chevrolet results are the values obtained by averaging from 4 to 6 results obtained at different laboratories (in a few cases where one result was far out of line, it was disregarded in compiling the averages). Oils B-1 and B-3 appear in Figure 8 under D number designations (D series Chevrolet results used for these two oils in Figure 8). Oils 1, 2, and 4 of the original series of seven reference oils are also included in the figure. Oils 5 (supply exhausted) and 3 (no reliable Chevrolet value available) were not included.

The relations between the results are shown both on a plain decimal scale and on a logarithmic scale. Of the sixteen oils included in the study, all showed satisfactory correlation between the two tests, except

Oil D-8. By the ISC test, D-8 should have been borderline in the Chevrolet test instead of bad.

Oil D-10. By the ISC test, D-10 should have been bad in the Chevrolet test instead of borderline.

Oil D-5. By the ISC test, D-5 should have been exceptionally good in the Chevrolet test instead of merely satisfactory.

To those who have followed closely previous attempts to establish correlation between laboratory bearing corrosion tests and engine tests, the correlation indicated in Figure 8 would appear remarkably good. In fact, the lack of reproducibility of the Chevrolet test results is almost sufficient to explain the deviations from the correlation—for example, one cooperating laboratory reported 0.26 gram bearing loss on oil D-8. If this result were used instead of the average of five results, point D-8 (Figure 8) would actually fall on the other side of the correlation curves.

DISCUSSION

Consideration of all the tests with the different catalysts leads to the generalizations indicated herewith:

The effect of the various solid catalysts varies widely, depending on the type of additive in the oil. The catalytic effect is complicated in some cases by chemical reaction of the catalyst with the additive.

Increasing the amount of catalyst used may either increase or decrease the bearing corrosion stability of various oils, depending on the type and concentration of additive present.

Lead oxide appears to be a particularly appropriate catalyst for use where correlation with the Chevrolet 36-hour test is desired. Such a correlation has been established using 0.5% lead oxide as catalyst.

If the above tests with lead oxide are of real significance with respect to the Chevrolet 36-hour test—that is, if they do include the most important conditions contributing to oxidation in the engine—then by analogy some of the limitations of the Chevrolet test can be recognized.

The variations in the Chevrolet 36-hour test results which are frequently obtained may well be due to variations in the rate of addition of lead catalysts from the fuel.

Since the Chevrolet test is extremely severe, it is probably true that oils which pass it will give satisfactory performance in ordinary heavy-duty service where leaded fuel is used. Oils which do not pass the Chevrolet test may or may not give satisfactory performance in such service. Oils will not necessarily rate in service in the same order as rated in the Chevrolet test, since the catalytic conditions, not to mention temperature, may be entirely different.

Oils which are good in the Chevrolet test will not necessarily be good in another type of engine test, of apparent equal severity and using the same fuel, since again the catalytic conditions may be entirely different.

Finally, Chevrolet bearing corrosion results are not generally applicable to Diesel tests, since nonleaded fuels are used in the latter.

Although apparently satisfactory correlation has been established between the Indiana stirring corrosion test and the Chevrolet 36-hour test for several oils, the test is not considered suitable for infallibly predicting performance of oils in the Chevrolet tests. In the first place, all the oils tested contained detergents. This limitation minimizes complications due to protective film formation both on the test strip in the beaker and on the bearings in the engine. Practically no background is available on the performance of nondetergent oils.

Furthermore, neither the Indiana stirring corrosion test nor any other beaker test exactly duplicates all the conditions affecting oil performance in the engine; and each oil may be affected to a different extent by each of these conditions—for example, (1) the continuous addition of lead catalysts and partially oxidized hydrocarbons from fuel blow-by, and (2) local hot spots which may either accelerate or retard (by activation of certain inhibitors) corrosion are conditions occurring in the Chevrolet test. When oils are encountered where such conditions have a major effect on the rate of oxidation (and corrosion), the absence of such conditions in the beaker test will cause that particular oil to deviate from any correlation that has been established for other oils.

ACKNOWLEDGMENT

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Analysis of Wood Sugars

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Experimental work in wood saccharification requires methods for the analysis of reducing sugar, fermentable sugars, and alcohol that are dependable, simple, rapid, and capable of being run in large numbers. Two methods were used for the determination of reducing sugars—one an electrometric titration method and the other a micromethod of Shaffer and Somogyi. The electrometric titration method was used when it was desirable to have a sugar analysis in as short a time as possible; the micromethod when large numbers of sugars were run or when concentrations and quantities available were too low for the macromethods. Fermentable sugars were estimated by determining the amount of sugar sorbed from a 1.5 mg. per ml. solution by a 5.0% yeast suspension. Alcohol was determined by the specific gravity method, using a Westphal balance with a thermostated container for the beer distillate. It was found that the surface tension error on the wire supporting the bob could be eliminated by the addition of a very small amount of a wetting agent.

IN STUDIES of wood saccharification it is necessary to have available analytical methods for the determination of the sugars produced, the amount of fermentable sugars, and the amount of alcohol produced when the wood sugars are fermented. Because wood sugars consist of mixtures of several sugars as well as dissolved lignin, furfural, formic and acetic acid, various oils, and other products in the wood, their analysis presents special problems. To be of most use in following the work, the analysis should be simple, rapid, and capable of being run in large numbers.

Two methods were used for the sugar determinations made at the Forest Products Laboratory: an electrometric titration method, where it was desirable to obtain analytical results as soon as possible; and the Shaffer and Somogyi method, where a large number of determinations were made simultaneously and small quantities were involved, but where it was not important to have the determinations completed in a short time.

Other methods were studied but rejected because of the time involved, the difficulty in observing the end point, or unreliable results.

Benedict's volumetric method (*3*) proved unsatisfactory because of the obscure end point. A volumetric hypoiodite method (*5*) was rapid but gave results that were frequently 50% higher than the Munson-Walker method (*2*), which, in turn, gave reliable results, but was time-consuming. An attempt was also made to use the Lane and Eynon volumetric method (*1*), but the color of the wood hydrolyzate in the presence of strongly alkaline Fehling's solution made it impossible to see the point at which the color of the methylene blue indicator disappeared.

DETERMINATION OF REDUCING SUGARS BY ELECTROMETRIC TITRATION

The determination of reducing sugars in wood hydrolysis by electrometric titration utilizes the titration of a standard Fehling's solution with reducing-sugar solutions as in the Lane and Eynon procedure (*1*) but avoids the difficulty with the determination of the end point. Britton and Phillips (*4*) have shown that the electromotive force across a normal calomel cell and a platinum electrode can be used to determine the end point in the titration of glucose with Fehling's solution. In their experiments the point of maximum inflection was the same as that point at which methylene blue is decolorized. Because they worked at a temperature of 90° C., however, they experienced difficulty with reoxidation by air, and the reaction was slow. In the Lane and Eynon procedure all but 1 or 2 ml. of the solution to be treated are added to the Fehling's solution, the mixture is brought to a boil and boiled for 2 minutes, and the titration is completed in a total boiling time of 3 minutes. Such a reaction was carried out in experiments at the laboratory, and the electromotive force across saturated calomel-platinum electrodes immersed in the solution was determined. The values for the electromotive force were plotted against the volumes of sugar solution to give the curve shown in Figure 1. The point of maximum inflection

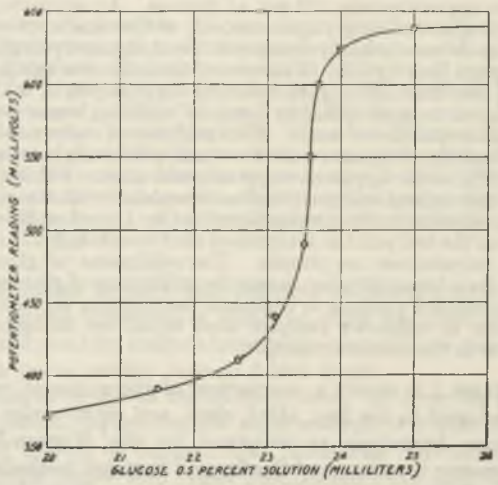

Figure 1. Electrometric Titration Curve for Glucose

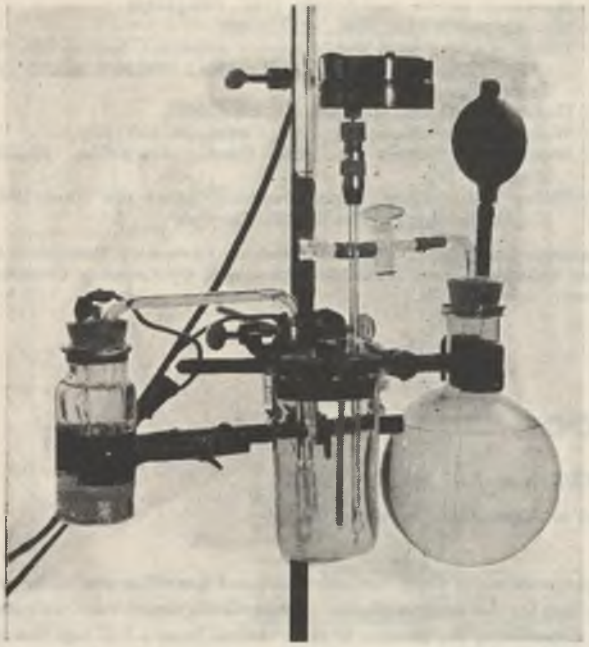

Figure 2. Electrometric Titration Apparatus

(−550 millivolts) was found to agree with the end point obtained with methylene blue when pure glucose solutions were used.

The reducing sugar content of dark-colored solutions may therefore be determined in the manner described by Lane and Eynon, except that the end point is determined electrometrically. This requires no more time than the original method in which an internal indicator is used, because the potentiometer readings may easily be taken in the intervals between additions of the sugar solution.

A more rapid method than this has been developed in which it is not required to clean and refill the buret for each determination nor to make an accurate dilution of the sample if the concentration is below 12 grams per 100 ml.

The apparatus for this determination is shown in Figure 2. The buret is arranged for automatic filling with a 5-mg. per ml. solution of glucose. Calomel and platinum electrodes are held firmly in place by the rubber stopper. After each determination, the ground-glass plug in the calomel cell is momentarily loosened to rinse it. A motor is provided for rapid stirring. The titrations are carried out in tall-form beakers held to the stopper by means of springs. A blank titration is made using 25 ml. of Soxhlet's modification of Fehling's solution. This amount of sugar reagent requires approximately 120 mg. of glucose. An estimate is then made of the reducing sugar content of the unknown sample. This can be conveniently done with wood sugars by multiplying the degrees Brix by 0.7. A volume of the unknown solution containing less than 120 mg. of reducing sugar is put in the beaker and diluted to approximately 5 mg. of reducing sugar per milliliter by the addition of water. This addition of water need not be done precisely, since an error of ±5 ml. will result in an error of only 0.3% in the apparent sugar concentration. Fehling's solution is then added and the titration completed with the standard glucose solution in the manner described by Lane and Eynon, except that the end point is determined electrometrically.

The calculations are simple. The milligrams of glucose required for a blank titration minus the milligrams of glucose added in the standard solution to complete the titration divided by the milliliters of unknown samples used equal the milligrams per milliliter in the unknown sample.

In Table I is shown a comparison of the apparent reducing sugar content in the first, third, sixth, and ninth cycles from a multistage hydrolysis as measured by the Munson-Walker, electrometric titration, and Shaffer and Somogyi methods. The Munson-Walker and electrometric titration methods show good agreement; the Shaffer and Somogyi method gave lower values.

Effect of Formic Acid on Electrometric Titration of Wood-Sugar Solutions. Kressman (*7*) found that formic acid is one of the decomposition products obtained in wood hydrolysis. When formic acid was added in varying quantities to the mixture being titrated, even in solutions containing equal parts of sugar and formic acid the volume of glucose solution required was not affected, but it did affect the shape of the titration curve, causing a more abrupt break from the horizontal to the vertical portion. The curve for the titration of the wood-sugar solutions also shows a more abrupt break than does pure glucose.

Effect of Calcium on Electrometric Titration. In certain samples of wood sugar that had been neutralized with lime it was found that the sharp breaks characteristic of pure glucose or raw wood hydrolyzates were lacking. Lane and Eynon (*8*) called attention to the fact that calcium, even in small quantities, adversely affects this titration, when methylene blue indicator is used, invariably resulting in low sugar values. A number of titrations were made in the presence of calcium to determine its effect on the electrometric titration curve. The curves are plotted in Figure 3. Curve 1 is the curve characteristic of pure glucose; curves 2, 3, 4, and 5 show the effect of 1, 3, 5, and 10 parts of calcium per 100 parts of glucose, respectively. These curves indicate that calcium must be removed from solutions containing more than 1% as much calcium as glucose before a satisfactory analysis can be made.

Lane and Eynon found that strontium and barium also interfere with the volumetric sugar determination when methylene blue is used as an internal indicator. This work confirms their findings and explains to a certain extent the reason for their difficulties. The decoloration of methylene blue is dependent on reaching a certain oxidation-reduction potential. Since the presence of calcium reduces the slope of the electromotive force

Table I. Comparison of Values for Per Cent of Reducing Sugars in Wood-Sugar Solutions Determined by Different Methods

Sample	Munson-Walker	Electrometric Titration	Shaffer-Somogy 30-Minute Heating
	%	%	%
Untreated			
19–1	5.77	5.70	5.40
19–3	3.48	3.47	3.17
19–6	2.31	2.31	2.16
19–9	1.82	1.80	1.71
Neutralized and clarified			
19–1	5.65	5.72	...
19–3	3.41	3.45	...
19–6	2.26	2.26	...
19–9	1.77	1.74	...

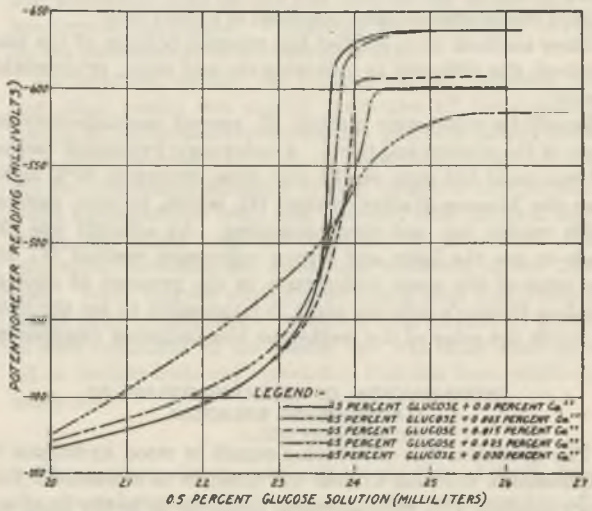

Figure 3. Effect of Calcium on Electrometric Titration of Fehling's Solution with Glucose

vs. sugar curve, it is apparent that it must make the end point less sharp. It is also apparent that if decoloration occurs at a point corresponding to an electromotive force more negative than −500 millivolts, the volume of sugar required is increased and the apparent sugar content is decreased, since the curves above this point are shifted to the right by the presence of calcium. The experience has been that the presence of calcium results in low sugar values. Calcium may be removed from neutralized worts by shaking the sample as received with 0.5% of its weight of powdered sodium or potassium oxalate and filtering or centrifuging out the precipitated calcium oxalate. The filtrate is then tested for calcium with more oxalate. If no precipitate forms, the sample is analyzed in the usual way. A moderate excess of oxalate is without effect on the reaction.

The volumetric titration for reducing sugars, using an electrometric end point rather than the usual internal indicator, has been used in approximately 3000 determinations in the work on wood hydrolysis and found to be dependable and very valuable where it is necessary to obtain an accurate analysis in a short time.

DETERMINATION OF REDUCING SUGARS BY SHAFFER AND SOMOGYI METHOD

The sugar analysis developed by Shaffer and Somogyi (*10*) has been found in other laboratories to give good service in the analysis of such materials as biological fluids and fermentation products. In recent work at the Forest Products Laboratory, the method has been found suitable for wood-sugar solutions and may be easily adapted to sugar concentrations as low as 0.2 mg. per ml.

Method Adopted for Analysis of Wood Sugars. The method adopted for the analysis of wood sugars is identical with that of Shaffer and Somogyi, using their reagent 50, and a 30-minute boiling time. The boiling time required was established by the following experiment:

Two-milliliter samples of the wood hydrolyzate obtained in the first cycle of a multiple-stage hydrolysis of spruce and of a composite sample from the same run were each diluted to 100 ml. One-milliliter samples of the diluted solutions were treated with sugar reagent 50 according to the Shaffer and Somogyi method and boiled for varying lengths of time.

In Figure 4 is shown on a percentage basis the reducing value plotted against time, using as 100% the value obtained in 30 minutes of boiling. It may be seen from these curves that the reducing value of the composite samples reached a maximum after 30 minutes of heating, while the value of the cycle 1 sample was still rising slowly. Because the slowly reducing materials are

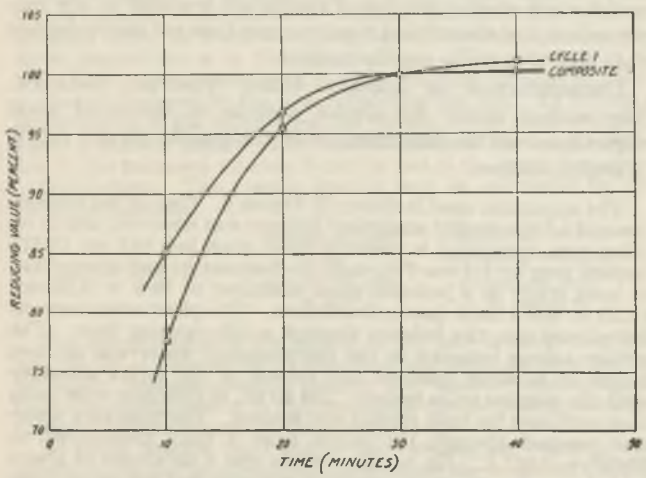

Figure 4. Reducing Value of Wood Hydrolyzates Heated with Shaffer and Somogyi Reagent 50

Table II. Relative Reducing Powers of Various Sugars toward Sugar Reagent

Sugar	Sample Used	Reducing Sugar Calculated as Glucose: Found by analyst A	Found by analyst B	Average
	Gram	*Gram*	*Gram*	*Gram*
d-Glucose	1.000	1.000	1.000	1.000
d-Xylose	1.000	0.930	0.926	0.928
d-Arabinose	1.000	0.760	0.760	0.760
d-Mannose	1.000	0.926	0.928	0.927
d-Galactose	1.000	0.814	0.816	0.815

concentrated in the first cycle, the reaction was not complete but sufficient for the work on saccharification and fermentation, and, therefore, a 30-minute heating period was used in all work involving the Shaffer-Somogyi method at this laboratory.

Determination of Reducing Power of Various Sugars toward Reagent. Wood sugar is a mixture containing primarily glucose mixed with smaller amounts of xylose, mannose, galactose, and arabinose. The relative amounts of these sugars vary with the species. In the work on hydrolysis, all wood-sugar yields are expressed in terms of *d*-glucose without taking account of differences in reducing power toward the sugar reagent.

Values for the relative reducing power of various sugars expressed as *d*-glucose as obtained by two different analysts are shown in Table II. Glucose has the highest reducing power of the sugars tested in spite of the fact that the pentoses have a higher percentage of reducing groups.

DETERMINATION OF FERMENTABLE SUGARS IN WOOD HYDROLYZATES

Wood hydrolyzates contain various hexoses, pentoses, sugar decomposition products, furfural, wood extractives, and lignin. Their value for alcohol production depends, however, on the fermentable sugar content and therefore it is essential that fermentable sugars be differentiated from unfermentable sugars and other reducing material. This may be done by the fermentation of a sample of the sugar followed by an alcohol determination, or by a determination of the sugar consumed in the process. These methods, however, are time-consuming, especially when applied to a large number of samples.

Methods of Estimating Fermentable Sugars in Dilute Solutions. It is well known that a high concentration of yeast will quantitatively remove sugar from dilute solutions at a rapid rate. In the examination of complex mixtures, such as blood or urine, fermentable sugars are estimated by determining the loss in reducing power of the sample after treatment with a high concentration of yeast (*11*).

Menzinsky (*9*) describes the use of this rapid yeast sorption method for the evaluation of the sugars contained in sulfite waste liquors. Hägglund (*6*) has found sulfite liquor from spruce to contain 17.0% pentoses, 42.7% mannose, 4.2% galactose, 3.2% galacturonic acid, 4.0% fructose, and 28.9% glucose. This distribution varies between species. Because galactose is not readily fermented unless the yeast has been previously acclimatized to its utilization, Menzinsky recommends that yeast for sulfite liquor analysis be acclimatized to galactose, or that the yeast be taken from a vat in which the fermentation of sulfite liquor is taking place.

In experiments at the Forest Products Laboratory on liquors obtained by the hydrolysis of wood, no effort was made to use acclimatized yeast for analysis because the proportion of galactose present is much smaller than in sulfite liquor.

Adjustment of pH of Sugar Solutions. In using the yeast sorption method for fermentable sugar analysis, it is desirable to have a pH slightly on the acid side. Menzinsky neutralized undiluted sulfite liquor with excess precipitated chalk and diluted the sample after filtration. This procedure is also satisfactory for use with wood hydrolyzates, but in order to avoid time required

for the filtration, approximately 0.1 ml. of concentrated sulfuric acid was added to 100 ml. of the diluted liquor to ensure the presence of more than 0.1% acid and then precipitated chalk was added in excess. Large variations in the amount of added acid or chalk have little effect on the pH of the resulting solution. In all the solutions tested, the pH in the presence of excess chalk was 6.3 ± 0.2.

Determination of Rate of Sorption of Fermentable Sugars from Diluted Wood Hydrolyzates by Yeast in High Concentrations. An experiment was devised to determine the rate at which the fermentable sugars in diluted wood hydrolyzates are "sorbed" by high yeast concentrations. Other workers have shown that sugar sorption is rapid and complete in the case of blood, urine, and sulfite liquor, but because of their complex nature it was desirable to determine this rate using acid-hydrolyzed wood sugars.

Four milliliters of a sample of a composite liquor from the early pilot-plant operations (experimental run No. 75) containing 3.95 grams of reducing sugar per 100 ml. were diluted to 100 ml. To this was added approximately 0.1 ml. of sulfuric acid from a calibrated dropper. Twenty milliliters of this solution were treated with excess calcium carbonate and 1 gram of a commercial compressed baker's yeast, shaken at 30° C. for various times, centrifuged, and analyzed. ("Red Star" compressed yeast was used in all the experiments reported in this paper.) The time allowed for sorption and the apparent fermentable sugar are plotted in Figure 5.

The sorption is complete in 1 hour and 1 hour, therefore, was chosen as the standard time of sorption.

Determination of Fermentable Sugar by Yeast Sorption. The sample to be analyzed for fermentable sugar is diluted to approximately 1.5 mg. of reducing sugar per milliliter. The reducing sugar content is determined by the Shaffer and Somogyi method, using reagent 50 with a heating period of 30 minutes; sulfuric acid is added to the diluted solution from a microburet in the proportions of approximately 0.1 ml. per 100 ml. Twenty milliliters of this solution are then put into a 30-ml. vial, and a sufficient quantity of precipitated chalk is added to leave a small amount of undissolved excess. Approximately 1 gram of compressed baker's yeast (*Saccharomyces cerevisiae*) is then added, and the vials are stoppered and shaken for 1 hour at 30° C. At the end of this time the vials are centrifuged, and a sample of the supernatant liquor is pipetted off and analyzed for sugar by the Shaffer and Somogyi method. If unwashed yeast is used, the value is corrected by subtracting the apparent sugar found in a blank determination. The difference in the sugar content of the solution before and after treatment with yeast corresponds to the fermentable sugar present.

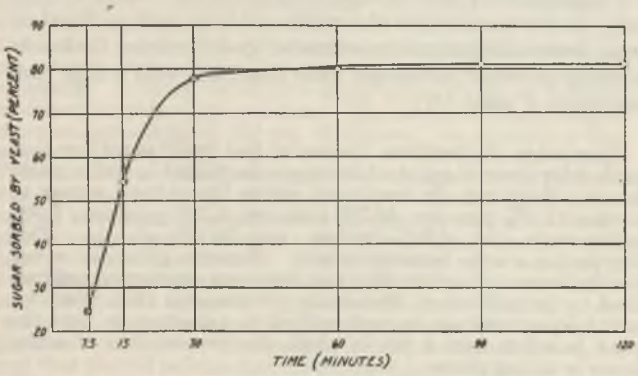

Figure 5. Sorption of Fermentable Sugars from Wood Hydrolyzates by 5% Suspension of Yeast

Comparison between Fermentability of Wood-Sugar Worts as Determined by Yeast Sorption and by Fermentation. A comparison was made between the fermentability of wood-sugar worts as determined by yeast sorption, and by fermentation of an 8-liter batch (Table III).

Over 100 fermentations in 8-liter batches using hydrolyzates from 15 different species of wood were checked by the yeast sorption method with essentially the same results.

Table III. Comparison between Fermentability of Wood-Sugar Worts as Determined by Fermentation and by Yeast Sorption

Run No.	Species	Fermentability, 8-Liter Fermentation	Fermentability, Yeast Sorption Method
		%	%
3	Spruce	72.9	74.6
4		74.0	73.4
5		72.5	71.6
8		76.2	74.2
9		75.1	73.5
19		76.0	76.4
20		75.5	75.3
21		76.5	75.0
47	Douglas-fir	77.9	77.4
48		81.0	81.1
49		81.3	80.6
50		81.4	82.3
51		81.2	80.8
52		82.0	80.0
53		80.8	79.3
54		80.5	79.2

DETERMINATION OF ALCOHOL IN FERMENTED WOOD-SUGAR WORTS

The fermentation of wood hydrolyzates or waste sulfite liquor produces a beer containing between 0.5 and 2.5% alcohol by weight. When analyzing solutions of this concentration, it is necessary to use controlled methods in order to get results of satisfactory accuracy.

Quantitative Removal of Alcohol from Beer by Distillation. In developing a procedure for the analysis of dilute alcohol solutions, it is important to know the minimum percentage of a beer that must be distilled in order to remove the alcohol quantitatively. By taking off this minimum percentage of the beer, a distillate of maximum concentration is obtained, resulting in greater accuracy in the final measurement.

By means of the equation of Virtanen and Pulkki (*12*) it can be shown that distilling off 45% of the initial volume of a beer will result in the removal of 99.9% of the alcohol.

Quantitative Determination of Alcohol. A number of techniques are available for the determination of alcohol in dilute solutions. Determinations of the specific gravity, refractive index, or the amount of dichromate required to oxidize the alcohol to acetic acid have all been used satisfactorily.

In work on wood sugars, the use of a refractive index method was avoided because of interference by furfural. The difference between the refractive index of furfural and water is eight times as great as the difference between the refractive index of alcohol and water. The error due to extraneous materials in the refractive index determination is seriously high. In the specific gravity method, slightly low uncorrected values are obtained. The dichromate oxidation method for the determination of ethanol is useful where small quantities of sample are available at low concentration, but the method requires more time per determination than does the specific gravity method.

Determination of Alcohol Using Westphal Balance. The method chosen for alcohol analysis of fermented wood sugars involved the determination of the specific gravity with a Westphal balance.

The apparatus used is shown in Figure 6. One of the balance pans of a high-quality analytical balance was removed, and in its place was suspended a mercury-filled glass bob 844 cm. (3.375 inches) long by 1.4 cm. ($^9/_{16}$ inch) in diameter in such a way that it hung freely in a jacketed glass container of 10.6 × 2.19 cm. (4.25 × 0.875 inch) inside dimensions. The glass container was introduced into the balance through a side-opening door. The rubber tubing bringing in the thermostated water was of such length as to allow removal and rinsing of the entire assembly with the solution to be tested. The 50 ml. of distillate were more than sufficient for both rinsing and testing. Thermostated water was pumped through the jacket from a bath maintained at 20.00° ± 0.01° C. On hot days there was a difference of about 0.1° C. between the temperature of the bath and the outlet from the jacket, but this differential was constant throughout the day's operations.

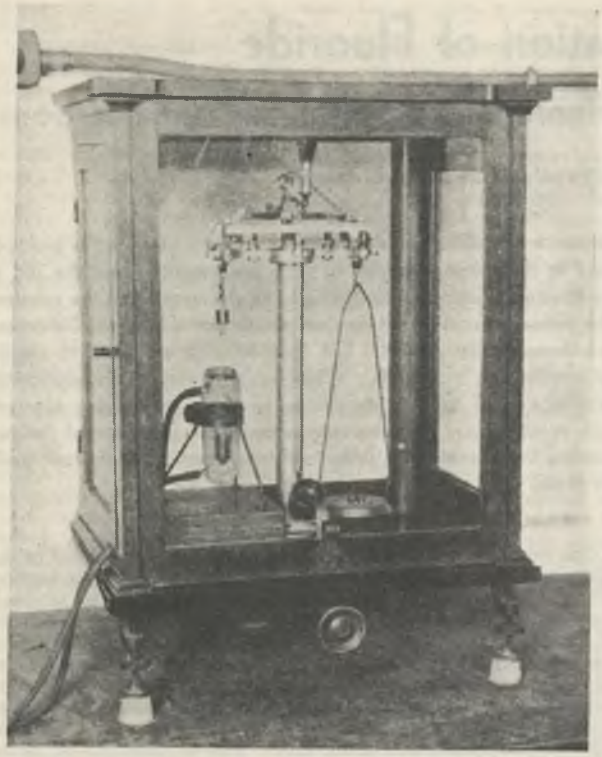

Figure 6. Westphal Balance and Jacketed Container

In the tests, the bob is weighed in air, in freshly boiled water, and in the solution that is to be analyzed. The loss in weight of the bob in the solution divided by the loss in weight in water gives the specific gravity. Because of a surface tension effect on the supporting wire the balance works less smoothly and a less reproducible rest point is obtained when water is used than when alcohol solutions are used. To overcome this difficulty with water and very dilute alcohol solutions, 1 ml. of a 0.8% solution of a wetting agent, Nacconol NR, is added to the water used for standardization and to the beer distillate before final adjustment of the volume. The effect of the Nacconol NR on the density of the alcohol solution is neglected in the calculations, since it is added in the same concentration to both the unknown solution and the water used for standardization.

PROCEDURE. *Distillation.* A 100-ml. sample of beer is pipetted into a 500-ml. round-bottomed flask, neutralized using a spot plate and bromothymol blue indicator, and distilled into a 50-ml. volumetric flask. After about 48 ml. have distilled, the distillation is interrupted and 1.00 ml. of 0.8% Nacconol NR is added. The volume is then adjusted to the mark. The volumetric flask containing the distillate is thermostated at 20° C.

Determination. The apparatus is standardized against water before each day's operations by weighing the bob in freshly boiled distilled water to which a wetting agent has been added in the same proportions as in the beer distillate. The container is always filled to the same level, so that the same amount of liquid is always displaced by the wire supporting the bob. To initiate a gentle swing of the balance pan on release, a rest point is chosen about 6 mm. off center. The determination of the weight of the bob in the unknown solution is carried out in the same manner.

Calculations. The specific gravity may be calculated by the following formula:

$$\text{Specific gravity} = \frac{\text{weight of bob in air} - \text{weight of bob in unknown solution}}{\text{weight of bob in air} - \text{weight of bob in water}}$$

The concentration of the alcohol in the beer in terms of grams per 100 ml. is determined by reference to a table showing the relationship between specific gravity and alcohol concentration. Since the concentration in the distillate is double that in the beer, the value obtained must be divided by 2.

To make routine calculations more rapid, the value of the weight of the bob in alcohol solutions minus the weight of the bob in water may be plotted as a function of the alcohol concentration in the beer to which it corresponds. In this way calculations are reduced to a simple subtraction and reference to a graph.

In order to correct for volatile material other than alcohol in the beer, an unfermented sample of the wood-sugar solution may be distilled and the percentage of apparent alcohol determined in the usual way. The alcohol concentration of the beer is then corrected by subtracting the apparent alcohol concentration of the wort before fermentation from the value obtained after fermentation. In the samples tested, this apparent alcohol concentration of the wort before fermentation has proved to be a small negative value.

The alcohol yield as determined by the specific gravity method may be checked by the use of an immersion refractometer, using the tables provided by the Association of Official Agricultural Chemists.

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Modified Dropping Funnel

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THE dropwise addition of compounds to stirred solutions is one of the most common synthetic organic chemistry operations. The funnel shown in the sketch has been found very useful in such operations. The funnel incorporates the leakproof stopcock designed by Newman with all the advantages pointed out by him (*1*). The pressure-equalizer feature permits exclusion of the atmosphere and minimizes the attention which the operator must give to maintain the desired addition rate. The off-center design of the funnel permits it to be mounted in a three-necked flask without interfering with the mercury seal generally contained in the middle neck. The vertical position of the stopcock ensures that it will not be dislodged by the vibration due to stirring.

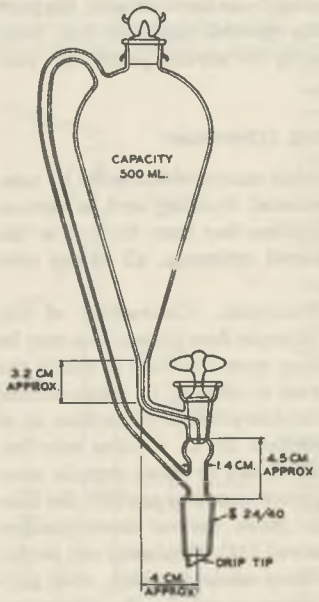

Figure 1. Modified Dropping Funnel

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Thorium Nitrate Titration of Fluoride

With Special Reference to Determining Fluorine and Sulfur in Hydrocarbons

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A method is described for determining fluorine by titration of fluoride with thorium nitrate, in the presence of sodium alizarin sulfonate, under optimum analytical conditions. The lamp technique for conversion of organic fluorine to fluoride is made quantitative by minimizing the surface between the combustion and absorption zones. Separation of fluoride from sulfate is avoided. The excess standard sodium carbonate absorbent is titrated with 0.05 *N* hydrochloric acid; the end point is sharpened by expelling carbon dioxide, and the buffer effect of sodium fluoride is taken into account. Acetic acid is used to adjust the initial pH for titration with 0.05 *N* thorium nitrate. Acetic acid also is incorporated in the thorium nitrate, in such concentration that the pH of the titration mixture is automatically so decreased that the relationship between fluoride and thorium nitrate titer is both rectilinear and stoichiometrically correct. The titration data are used to correct for interference by sulfate. When sulfur is absent, the acidimetric titration can be used to determine another acid-forming element, such as chlorine. A composite nomograph is presented for calculating the fluorine and sulfur contents. Typical analytical results are given.

THE method described herein is an outcome of research directed to the use of fluorine-containing catalysts, during the course of which considerable fundamental information relating to the thorium nitrate titration of fluoride was accumulated. Although developed primarily to meet the need for determining up to about 0.1% of organically combined fluorine in hydrocarbons, such as those present in various stages of the manufacture of aviation gasoline by hydrofluoric acid alkylation (*13*), this method should prove useful for the analysis of many other materials from which the fluorine can be obtained as a fluoride solution, provided conditions indicated as being essential are observed. In comparison with earlier thorium nitrate methods of determining fluoride, it possesses advantages of simplicity, wide range, accuracy, and reproducibility by various analysts; in addition, it determines with reasonable accuracy another acid-forming element, such as sulfur or a halogen other than fluorine.

PRINCIPLE OF METHOD

In general, the principle of this method is that of converting the fluorine and the sulfur in a sample into an aqueous solution of fluoride and sulfate, determining the total acid equivalent to the fluoride and the sulfate, determining specifically the fluoride by titration with thorium nitrate under selected conditions, and calculating the sulfur after deducting from the total acid the part equivalent to the fluorine. This general principle has been satisfactorily used in this laboratory for several years with various specific titration techniques.

OPTIMUM GENERAL CONDITIONS

To facilitate obtaining dependably comparable results by analysts of various degrees of professional training, and in various laboratories, each analytical condition has been limited to the one particular choice that appeared optimum, all things considered.

CONVERSION TO FLUORIDE SOLUTION. Conversion of the fluorine-containing sample to an aqueous fluoride solution may be effected in various ways, depending upon the form in which the fluorine exists. When the fluorine is already in water-soluble form, all that may be necessary is absorption or extraction, as of hydrofluoric acid from a hydrocarbon by an alkaline solution. When the fluorine is in the form of one or more organic compounds, the compounds must be decomposed to convert the fluorine to a water-soluble fluoride. Since various decomposition methods have been recently reviewed (*12*), they need not be discussed in detail, except for the lamp method, which, with suitable modification in apparatus, serves as well for the determination of organic fluorine as it has served for many years for the determination of organic sulfur.

One form of the lamp apparatus (*11*, *23*) has been used in this laboratory for the determination of fluorine in hydrocarbons with reasonably satisfactory results for several years, although the results from known mixtures indicated that the recovery of fluorine was usually low for fluorine contents above 0.05% and high for fluorine contents below this value. Recently, another form of the lamp apparatus was reported as giving low and somewhat erratic results, which were accompanied by severe etching of the glass of the collecting chimney and of the inlet tube of the absorption flask (*26*). The appearance of severe etching may be caused by a siliceous fluorine-containing deposit, such as that observed in the distillation of fluoride as fluosilicic acid (*15*, *20*, *21*). In this laboratory, a similar deposit has been observed many times in glass columns used for fractional distillation of hydrocarbons containing organic fluorine. A light deposit has also been observed a few times, when a hydrocarbon of exceptionally high fluorine content was being burned, in the outlet of the chimney of the lamp apparatus; but no other evidence of etching has been observed, even after repeated use of the lamp apparatus. Significantly, "adsorbed silicon fluoride" must be desorbed in a method employing combustion in a heated silica tube (*7*, *16*). Hence, the etchinglike deposit, which usually is so small as to be invisible, seemed responsible for the somewhat inexact results heretofore obtained by the lamp method.

Confirming this view, elimination of substantially all surface between the combustion and absorption zones made the recovery of fluorine quantitative. In addition, the apparatus was simplified; the chimney became merely a downward extension of the absorption tube, as is illustrated in Figure 1. The rubber stopper required in the original apparatus (*11*, *23*) to connect the chimney, the Erlenmeyer flask, and the absorption tube was eliminated; this stopper was troublesome because it deteriorated rapidly, causing leakage unless replaced after every few combustions.

In the new apparatus, a noticeable salt deposit is likely to form on the under surface of the disk, apparently because of creeping of the absorbent through the hot disk. To obviate loss of particles of this deposit that might be dislodged during removal of the lamp at the end of the combustion, the apparatus may be constructed with two disks about 20 mm. apart; the lower disk, which may be extra coarse, advantageously also dissipates a large part of the heat of combustion by radiation. However, the single-disk apparatus is fully satisfactory, especially if a clean sheet of paper, preferably black and glossy, is used beneath the apparatus to recover any dislodged particles.

The combustion must be complete, or smokeless. Incomplete combustion leads to low fluorine values because of incomplete decomposition of the fluorine compound, to high sulfur values because of formation of organic acids, and to difficulty in the titrations because of discoloration by colloidal carbon. The combustion should be in a synthetic atmosphere of oxygen and carbon dioxide (*23*), rather than in purified air, to obviate the error (in the sulfur determination only) resulting from oxidation of nitrogen (*1*, *23*). The flow rate of the atmosphere through the lamp need not exceed 0.7 liter per minute if the oxygen content is about 40% by volume. The carbon dioxide must be free from sulfur compounds; testing each fresh cylinder for hydrogen sulfide and for sulfur dioxide is desirable. Under the absorption conditions used, any sulfur dioxide that may be formed in the combustion is completely oxidized; adding hydrogen peroxide to the absorbent is unnecessary and is undesirable, for the peroxide, which decolorizes the indicator, cannot be

readily destroyed by boiling unless the solution is excessively alkaline.

VOLUME OF ABSORBENT. To minimize the volume of standard hydrochloric acid required in titrating the excess absorbent, the volume of absorbent should be limited to the minimum consistent with good analytical technique. Analyses of synthetic mixtures of isooctane and fluorobenzene showed that 10 ml. of 0.05 *N* sodium carbonate in an absorber in which all the absorbent rests upon a fritted-glass disk are adequate; no fluoride was found in a second absorber in series with the first. Accordingly, this volume, which is stoichiometrically equivalent to 10 mg. of hydrogen fluoride, or to the fluorine in 9.5 grams of a material containing 0.10% of fluorine, is preferred. To compensate for vaporization of water, an approximately equal volume of water is added, preferably before introduction of the absorbent, when it can serve to indicate whether the assembly is sufficiently leak-free to retain the absorbent upon the fritted-glass disk.

SEPARATION FROM INTERFERING SUBSTANCES. In the determination of fluorine in some materials by titration of fluoride with thorium nitrate, the fluoride may have to be preliminarily separated from interfering substances by an appropriate technique (*3, 5, 9, 10, 14, 15, 17, 18, 21, 25*). Obviously, whenever possible, separation should be avoided, for it is time-consuming and troublesome. When, as is true for most hydrocarbons, no acid-forming element other than fluorine, sulfur, and oxygen is present, so that the only interfering substance is sulfate, separation is advantageously avoided by determining the sulfur content acidimetrically and correcting the thorium nitrate titer correspondingly.

DILUTING AND ALIQUOTING. In an early precursor of this method that generally resembled published fluoride-titration techniques (*3, 14, 18, 21, 22, 24*), it was necessary to dilute the analytical solution until it contained not over 2.5 mg. of fluoride per 100 ml. and to take, for titration, a 10-ml. aliquot. Improvements here described have led to the elimination of this diluting-and-aliquoting step, which required some judgment as to the extent of the diluting and entailed the possibility of being omitted with sacrifice of accuracy.

TITRATION VESSEL. The most satisfactory titration vessel is a 125-ml. Erlenmeyer flask, which is advantageously adapted for mixing of the titration mixture by swirling. It preferably should be provided with a mark indicating a volume of 50 ml. When several flasks are used interchangeably, all should be optically alike.

VOLUME OF TITRATION MIXTURE. The most convenient volume for titration in a 125-ml. Erlenmeyer flask is approximately 50 ml., which is also roughly the volume of the absorbent and washings. In the titration with thorium nitrate, the initial volume must be fairly close to this value, at least within 5 ml., for the results vary with the concentration of the indicator and with the volume being titrated (*21*).

STRENGTH OF REAGENTS. For convenience, the strength of the reagents is the same as that in a current acidimetric lamp method for sulfur (*23*), 0.0500 *N*. For simplicity, and to obviate the possibility of having alternative procedures that might lead to divergent results by different analysts, only one strength of each reagent is used.

STRENGTH OF INDICATOR. What was judged to be the optimum amount of sodium alizarin sulfonate as indicator was experimentally determined, and the strength of the indicator was selected to be 0.025% in order that this amount would be measured and added by a 1-ml. pipet. The resulting concentration of indicator in the titration mixture coincides with that used by Reynolds and Hill (*21*); it is intermediate between that used by Rowley and Churchill (*22*) and that used by Armstrong (*3*).

HYDROCHLORIC ACID TITRATION. The titration of excess absorbent with hydrochloric acid differs from that in the aforementioned acidimetric method for sulfur (*23*) in two main respects:

1. The indicator is sodium alizarin sulfonate instead of methyl orange. Primarily, sodium alizarin sulfonate is used because it is the indicator required in the subsequent titration with thorium nitrate. The color changes in a pH range only slightly above that for methyl orange, being yellow at a pH of 4.24 and perceptibly pink at a pH of 5.28. The amount of indicator is the same as that required for the titration with thorium nitrate, in order that only one addition of indicator need be made during the entire analysis.

2. The sharpness of the end point is improved by expelling carbon dioxide by boiling. Removal of all carbon dioxide is not necessary and should not be attempted; long-continued, progressive acidification and boiling causes loss of fluoride, if present. The preferred procedure is: (1) boiling the alkaline solution, primarily to concentrate it, if necessary, to about 40 ml. but also to remove readily expellable carbon dioxide; (2) titrating with hydrochloric acid to a preliminary end point; (3) boiling for about 2 minutes to remove additional carbon dioxide; and (4) titrating to the final end point, which is exceedingly sharp except when much fluoride is present.

The preferred rate of boiling is rather high, being sufficient to vaporize about 2 ml. of water per minute or to cause an added glass ball or bead, about 4 mm. in diameter, to dance about, making a clearly audible continual tinkling.

When sulfur is known to be absent, the boiling can be omitted. However, as is indicated below, when boiling is omitted, the presence of considerable carbon dioxide decreases the amount of hydrochloric acid added, with the result that, when the fluoride is in excess of a few milligrams, the thorium nitrate titer is decreased slightly.

COLOR STANDARDS. Although the ability to judge the end point in the thorium nitrate titration is readily acquired, a permanent color standard (*10*) is useful in ensuring that the same end point is used by various analysts, in various laboratories. Accordingly, a color standard was developed from sodium chromate and cobalt nitrate. Experience has shown that the sodium chromate must be the C.P. tetrahydrate; other forms of sodium chromate, in chemically equivalent amount, do not always give the proper color. From the same stock solutions, a color standard was also developed for the hydrochloric acid titration.

THORIUM NITRATE TITRATION

END POINT. The exact tint at the end point in the thorium nitrate titration optimally should be one that can be readily judged by most persons. A faint pink end point, which cannot be judged at all by many persons, is unsatisfactory for routine analyses. It is highly sensitive to variations in light, appearing differently to different persons and even to the same person on different days; in consequence, it requires considerable experience, the use of a color standard freshly made with precisely measured volumes of standard solutions of sodium fluoride and thorium nitrate, and much time and patience for color matching.

The relatively deep pink tint selected for the end point of this method is that at which the rate of change of color with addition of thorium nitrate was experimentally found to be the most rapid. This tint, which is judged comparatively without difficulty, is substantially visually uniform for all amounts of fluoride; although the presence of a precipitate affects the appearance of the titration mixture noticeably, the eye is able to judge the end point accurately and reproducibly, provided that the mixture is swirled to keep the precipitate in suspension. The possible alternative technique of letting the precipitate settle and judging the end point by the appearance of the precipitate, which adsorbs the indicator, is relatively inferior.

The titration mixture should be compared with the color standard in uniform light. Artificial light is superior to natural daylight, which fluctuates too much. The optimum light appears to be the slightly reddish yellow light from an incandescent electric lamp, which is preferably above or behind the observer, so that the mixtures are viewed, optimally against a glare-free neutral gray background, by reflected light rather than by transmitted light. However, in view of its popularity for other titrations, a "fluorescent titration support" was used in the present investigation.

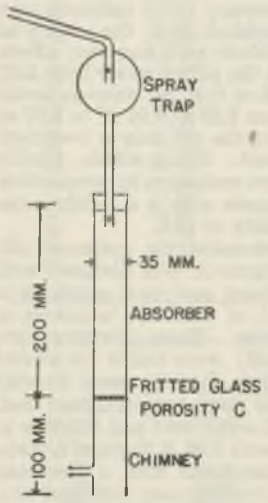

Figure 1. Absorption Apparatus

ACIDITY. In the titration of fluoride with thorium nitrate, the acidity of the titration mixture must be closely controlled. In early forms of the thorium nitrate method, the acidity was adjusted with a slight excess of dilute hydrochloric acid (*4, 5, 25*); in recent forms, with a buffer made by half-neutralizing monochloroacetic acid with sodium hydroxide (*3, 10, 14, 15, 18, 21, 22, 24*). However, neither the influence of the acidity on the analytical result nor the technique of controlling the acidity, beyond measurements of the pH obtained with the chloroacetate

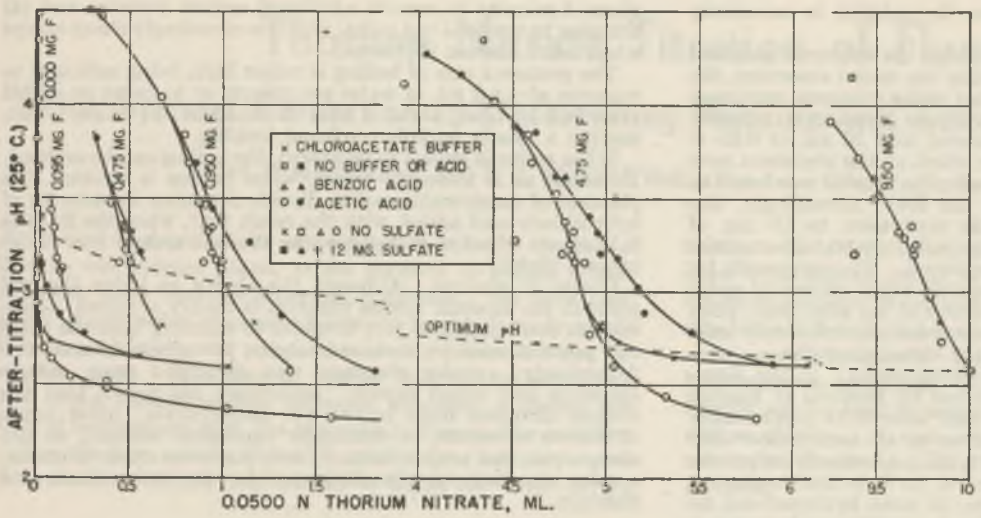

Figure 2. Titration of Fluoride with Thorium Nitrate

buffer (*15*, *21*, *22*) and with other buffers (*3*, *8*), appears to have been previously adequately investigated.

ACIDITY-CONTROL AGENT. Experience indicated that the chloroacetate buffer is not fully satisfactory as an acidity-control agent, for different preparations differed noticeably in behavior—for example, when different preparations were used, the volume of 0.05 *N* thorium nitrate required for zero fluoride varied from 0.020 to 0.065 ml. The variation was traced to the establishment of too low a pH range, in which the thorium nitrate required for zero fluoride varies markedly with slight variation in pH. Slight variations in the pH established by different preparations of the buffer may be attributed to such possible factors as different proportions of one or more impurities (perhaps polychloroacetic acids) and slightly different ratios of acid to salt. Obtaining a pH range that is generally too low may be attributed to such factors as using too much of the buffer, having too high a ratio of acid to salt in the buffer, and neglecting the pH-depressing effect of salts of relatively strong acids (hydrochloric, sulfuric, nitric) that are originally present or are formed during the titration. Another possibly pertinent factor is the formation of a flocculent brownish precipitate on aging of the buffer. These factors, which indicate the complexity associated with the chloroacetate buffer, were not investigated; instead, a relatively simple and advantageous pH-control technique was developed that is substantially free from these factors, and from the recent specification that the buffer should be prepared fresh each week (*24*).

In earlier methods, no extraneous acid or alkali is added during the titration, for 0.05 *N* thorium nitrate itself has approximately the same pH, 2.8, as that established by the choroacetate buffer (*3*, *15*, *21*). Thus, the primary function of the buffer has been that of adjusting the initial acidity of the analytical solution. Indeed, addition of a buffer is unnecessary (*3*) if sufficient care is taken to adjust, with dilute hydrochloric acid, the acidity of the solution before titration. Hydrochloric acid, however, affects the acidity too strongly. It changes the pH of water from 3.01 at a concentration of 0.001 *M* to 2.02 at 0.01 *M*, whereas acetic acid changes the pH of water only from 3.37 at 0.01 *M* to 2.87 at 0.1 *M* (*6*)—that is, acetic acid affects the pH only a twentieth as strongly as does hydrochloric acid. Being stable, readily obtainable in high purity, and free from variations in composition attributable to half-neutralization, acetic acid is a highly satisfactory agent for controlling the acidity or pH.

OPTIMUM pH. In a search to determine the optimum pH, many data, which are presented in Figure 2, were obtained with 50-ml. synthetic mixtures that simulated analytical solutions in containing an aggregate of 10.00 ml. of 0.0500 *N* solutions of sodium carbonate and sodium fluoride. These mixtures were titrated with 0.05 *N* hydrochloric acid; were boiled for several minutes to remove most of the carbon dioxide; were titrated again while still hot; were cooled to room temperature; and, after addition of various amounts of acetic acid and dilution to approximately 50 ml., were titrated with 0.05 *N* thorium nitrate. After the titration, the pH was measured with a Beckman industrial model pH meter, and the reading was corrected to a temperature of 25° C. For comparison, Figure 2 includes some data obtained by the use of the chloroacetate buffer, of no buffer or excess acid, and of benzoic acid.

The data provide a useful correlation between pH and thorium nitrate titer. From the left-most curve in Figure 2, it is apparent that, for small amounts of fluoride, the lower limit for the pH should not be much below 3.0. Below this pH, the thorium nitrate required for zero fluoride progressively increased, rapidly becoming excessively large; above this pH, the thorium nitrate was constant at 0.010 to 0.015 ml. (readings were made to the nearest 0.005 ml.). Aside from stoichiometric requirements, a practical upper limit is determined by the fact that, for considerable amounts of fluoride, the end point is indistinct (*22*) above a pH of 3.5, requiring "building up" to the proper intensity.

Obviously, the optimum pH should be such that the relationship between fluoride and thorium nitrate is rectilinear. When the chloroacetate buffer is used, this relationship has been reported to depart from a straight line in the vicinity of 0.1 mg. of fluoride (*21*); the divergence from a straight line is detectable, however, for much larger amounts. From the geometrical relationships of the curves in Figure 2 for various amounts of sulfate-free fluoride (0.000, 0.100, 0.500, 1.000, 5.00, and 10.00 ml. of 0.0500 *N* sodium fluoride), it may be seen that there is no pH at which this divergence vanishes for so large a range as 0 to 10 mg. of fluoride. The nearest approach to a single-valued optimum pH is 3.30, inasmuch as the divergence is in one direction for lower values and in the opposite direction for higher values. But, at this pH, the divergence practically vanishes for only the range of 0 to 1 mg. of fluoride, so that the relationship between fluoride and thorium nitrate is rectilinear for an undesirably limited range; furthermore, although rectilinear, this relationship is not stoichiometrically correct.

Instead of attempting to maintain a single pH, an advantageous alternative is so changing the pH during the titration that the relationship between fluoride and thorium nitrate is both rectilinear and stoichiometrically correct. According to this alternative, the pH must follow the path indicated by the broken transverse line in Figure 2—that is, the optimum pH, as defined by this path, decreases from an initial value of approximately 3.35 in correspondence with the amount of fluoride present.

CONTROL OF pH. The pH can be automatically decreased during the titration by incorporating acetic acid in the thorium nitrate solution, which otherwise, because of its diluting effect, increases the pH slightly. From an experimental correlation between pH and concentration, the appropriate concentration of acetic acid, for 0.05 *N* thorium nitrate, was found to be 1.2 *M*.

Accordingly, in this method, the pH is controlled by adding to the 50-ml. analytical solution, after the titration with 0.05 *N* hydrochloric acid, 1 ml. of 0.40 *M* acetic acid, to bring the pH to the proper initial value; and by using as the titrating reagent a 0.0500 *N* (or 0.0125 *M*) solution of thorium nitrate in 1.2 *M* acetic acid. The manipulations required during a determination are identical with those required when the chloroacetate buffer is used.

TITRATION BLANK. In this method the so-called titration blank, which is the volume of thorium nitrate solution required for zero fluoride, is determined directly and once for all, inasmuch as it is constant and is identical with the experimental value. In this respect, it differs advantageously from that in methods in which it is found by extrapolation (*3*, *21*, *24*); furthermore, it is free from the inaccuracy present when either of the two known amounts of fluoride that must be titrated in the extrapolation methods differs considerably from the amount in the analytical solution itself.

TEMPERATURE OF TITRATION. Although an increase in temperature decreases slightly the thorium nitrate titer (*21*), the decrease is so small that cooling the solution, after expelling carbon dioxide, is not necessary.

STANDARDIZATION OF THORIUM NITRATE. For routine analyses, standardization of the thorium nitrate does not appear to be necessary when this solution is made from the C.P. tetrahydrate, but it is necessary when the solution is made from the dodecahydrate, which varies appreciably in water content. The standardization preferably should be made by titration

Table I. Correlation of Fluoride and Thorium Nitrate

Solution	0.0500 *N* Na_2CO_3	0.0500 *N* NaF	Fluorine Present	0.0500 *N* HCl	0.0500 *N* $Th(NO_3)_4$ in 1.2 *M* HOAc
	Ml.	*Ml.*	*Mg.*	*Ml.*	*Ml.*
1	10.00	0.000	0.0000	10.00	0.010
2	9.99	0.010	0.0095	9.99	0.020
3	9.95	0.050	0.0475	9.95	0.060
4	9.90	0.100	0.095	9.90	0.110
5	9.50	0.500	0.475	9.52	0.510
6	9.00	1.000	0.950	9.04	1.010
7	5.00	5.00	4.75	5.22	5.01
8	0.00	10.00	9.50	0.45	10.01
9	0.00	20.00	19.00	1.05	20.02
10	0.00	30.00	27.50	1.62	30.3
11	0.00	50.00	47.50	3.80	50.5

against 0.05 *N* sodium fluoride rather than by precipitation as the oxalate and ignition to thoria (*15*, *24*), which is likely to give low results because of solubility of the oxalate, especially in acidic solutions. For precise work, either the solution should be standardized or the salt should be preliminarily analyzed by ignition to thoria, for even the tetrahydrate varies slightly in water content.

The data of Table I demonstrate the rectilinear and stoichiometric correctness of this method. Appreciable divergence, apparently because of depletion of the indicator by dilution and by adsorption by the precipitated thorium fluoride, begins only when the fluoride exceeds about 20 mg.

INTERFERENCE BY SULFATE. The interference by sulfate has been reported to result in an error of 0.015 mg. of fluorine for 2 mg. of sulfate (*21*). From data in Figure 2 that were obtained with synthetic mixtures containing 12 mg. of sulfate (5.00 ml. of 0.0500 *N* sulfuric acid), it is apparent that the interference depends not only on the amount of sulfate but also on the amount of fluoride and on the pH. In fact, at sufficiently high pH, the interference disappears; but use of such high pH is undesirable because it makes the end point indistinct and the relationship between fluoride and thorium nitrate neither rectilinear nor stoichiometrically correct. It may be noted, from the pH relationships discernible in Figure 2, that, in comparison with a method using a constant pH of about 2.8, this method decreases markedly the interference by sulfate for small amounts of fluoride, below about 3 or 4 mg. Additional correlative data, obtained with synthetic mixtures, are given in Table II.

A simple method of correcting for the interference by sulfate is described below.

INTERFERENCE BY SODIUM SALTS. Two divergent, puzzling types of sodium-salt interference have been reported (*21*); both types are readily understood in the light of the present investigation. Only one of these types can be detected when acetic acid is used in lieu of the chloroacetate buffer. This type is due to the depressing effect of the sodium salt on the pH. The data of Table III, which were obtained with preliminary addition of various amounts of sodium chloride, follow within experimental error the corresponding curves of Figure 2—that is, the thorium nitrate titer increased in correspondence with decrease in pH. When the sodium salt is derived from the use of 0.05 *N* sodium carbonate as an absorbent, this type of interference is negligible, for 10 ml. of this solution corresponds to less than 30 mg. of sodium chloride.

The other type of interference was found to be only apparently caused by the sodium salt, being really due to an interfering effect of the chloroacetate buffer. This effect is illustrated by data in Figure 2, for 0 and 4.75 mg. of fluoride, that were obtained by the use of 0.5, 1, 2, 5, and 10 ml. of the buffer (0.5 *M* chloroacetic acid, 0.5 *M* sodium chloroacetate); corresponding to progressive decrease in pH with increase in amount of buffer, the relationship between thorium nitrate and posttitration pH abruptly changed from that found by the use of acetic acid in the absence of sulfate to approximately that found by the use of acetic acid in the presence of 12 mg. of sulfate. As is shown by the data of Table IV, in accordance with the type of sodium-salt interference already discussed, the addition of 1000 mg. of sodium chloride depressed the pH and increased the thorium nitrate titer. But, for any particular posttitration pH, the addition apparently decreased the titer, markedly so for zero fluoride. For example, in an extreme instance, for a pH of 2.59, in the absence of fluoride, the thorium nitrate titer appeared to decrease from 1.040 to 0.165 ml. In reality, the apparent decrease was due to the fact that the smaller titer was for a solution having the smaller amount of buffer and consequently the smaller interfering effect.

INTERFERENCE BY SILICA, EVAPORATION, ETC. Some puzzling interfering effects reported in the literature are explainable in the light of the correlationship between pH and thorium nitrate titer that is presented by Figure 2. Concentration by evaporation of alkaline (phenolphthalein) sodium fluoride solutions led to low thorium nitrate titers when silica, added as sodium silicate, was present (*21*, Table II); this effect appears to have been due to an increase in pH by the sodium silicate, for the solution apparently was not titrated with an acid before addition of the chloroacetate buffer. This view is strengthened by the fact that, when the sodium silicate was equivalent to so much as 7.6 mg. of silica, there was observed an indistinct end point, which indicates a pH of 3.5 or more. Evaporation of perchloric acid distillates from phosphate rock led to relatively slightly low titers (*21*, Table III); this effect appears to have been due to increase in pH by removal of acid that had been carried over (*10*) in the distillation. Blank distillates from perchloric acid consumed more thorium nitrate than was required by the titration blank (*21*, Table IV); this effect appears to have been due to increase in pH by acid carried over (*10*) in the distillation.

As is obvious from either Figure 2 or Table IV, the thorium nitrate titer is exceedingly sensitive to slight pH changes in the region for which the chloroacetate buffer was designed. No reliance should be placed on the buffer action of the chloroacetate buffer to counteract any acid or alkali; addition of this buffer, if used at all, should be preceded by a rough adjustment of acidity with dilute acid or alkali. This precaution must also be observed when acetic acid is used. In this connection, the data of Table V are of interest, inasmuch as they indicate the influence of unexpelled carbon dioxide.

Table II. Correlation of Sulfate, Fluoride, and Thorium Nitrate

Solution	0.0500 *N* Na_2CO_3	0.0500 *N* NaF	0.0500 *N* H_2SO_4	0.0500 *N* $Th(NO_3)_4$ in 1.2 *M* HOAc
	Ml.	*Ml.*	*Ml.*	*Ml.*
12	5.00	5.00	1.00	5.17
13	5.00	5.00	2.00	5.28
14	5.00	5.00	3.00	5.36
15	5.00	5.00	4.00	5.49
16	5.00	5.00	5.00	5.64
17	10.00	0.00	5.00	0.030
18	9.00	1.00	5.00	1.17
19	8.00	2.00	5.00	2.29
20	7.00	3.00	5.00	3.43
21	6.00	4.00	5.00	4.52
22	20.00	0.00	0.00	0.010
23	10.00	10.00	0.00	10.07
24	15.00	5.00	5.00	5.64
25	15.00	5.00	10.00	5.86
26	15.00	5.00	15.00	6.05
27	10.00	10.00	5.00	10.98
28	5.00	15.00	5.00	16.51

Table III. Correlation of Sodium Chloride with pH and Thorium Nitrate

NaCl Added	No Fluoride Present		4.75 Mg. of Fluoride Present	
	pH (25° C.)	$Th(NO_3)_4$[a]	pH (25° C.)	$Th(NO_3)_4$[a]
Mg.		*Ml.*		*Ml.*
0	3.36	0.010	2.85	4.97
85	3.33	0.015	2.82	4.99
985	3.21	0.010	2.71	5.06
4985	2.99	0.015	2.45	5.12

[a] 0.0500 *N*, in 1.2 *M* acetic acid.

Table IV. Correlations of Sodium Chloride and of Chloroacetate Buffer with pH and Thorium Nitrate

	No Fluoride Present				4.75 Mg. of Fluoride Present			
	No NaCl Added		1000 Mg. of NaCl Added		No NaCl Added		1000 Mg. of NaCl Added	
Buffer Added	pH (25° C.)	$Th(NO_3)_4$[a]	pH (25° C.)	$Th(NO_3)_4$[a]	pH (25° C.)	$Th(NO_3)_4$[a]	pH (25° C.)	$Th(NO_3)_4$[a]
Ml.		*Ml.*		*Ml.*		*Ml.*		*Ml.*
0.5	2.88	0.020	2.78	0.035	2.92	4.90	2.80	4.90
1.0	2.79	0.030	2.67	0.065	2.80	4.97	2.70	5.07
2.0	2.73	0.080	2.59	0.165	2.74	5.07	2.64	5.20
5.0	2.65	0.555	2.52	0.790	2.65	5.37	2.57	5.58
10.0	2.59	1.040	2.47	2.47	2.61	6.09	2.54	6.30

[a] 0.0500 *N*, in 1.2 *M* acetic acid.

Table V. Influence of Boiling on Thorium Nitrate Titer

Boiling Period	0.0500 *N* HCl Used			0.0500 *N* $Th(NO_3)_4$ in 1.2 *M* HOAc	Av. Titer
	Cold	Hot	Total		
Min.	*Ml.*	*Ml.*	*Ml.*	*Ml.*	*Ml.*
CO_2-saturated mixture of 5.00 ml. of 0.0500 *N* Na_2CO_3 + 5.00 ml. of 0.0500 *N* NaF					
0	4.80	..	4.80	4.97	
0	4.81	..	4.81	4.99	4.967
0	4.84	..	4.84	4.94	
5	4.85	0.32	5.17	4.99	
5	4.86	0.27	5.13	4.97	4.973
15	4.84	0.35	5.19	4.96	
5	..	5.00	5.00	5.00	
5	..	5.00	5.00	5.00	5.020
15	..	5.20	5.20	5.06	
CO_2-saturated mixture of 8.33 ml. of 0.0500 *N* Na_2CO_3 + 5.00 ml. of 0.0083 *M* Na_2SiF_6					
0	5.10	..	5.10	4.90	
0	5.02	..	5.02	4.93	4.917
0	4.99	..	4.99	4.92	
5	4.77	0.35	5.12	4.96	
5	4.78	0.38	5.16	4.92	4.943
15	4.85	0.48	5.23	4.95	
5	..	5.12	5.12	4.99	
5	..	5.18	5.18	4.97	4.967
15	..	5.17	5.17	4.94	

These data were obtained primarily to test whether appreciable fluoride is lost during the boiling to expel carbon dioxide. They were obtained with two sets of carbon dioxide–saturated synthetic mixtures, which simulated analytical solutions such as might be obtained by absorption, in 10 ml. of 0.05 *N* sodium carbonate, of approximately 4.75 mg. of fluorine as hydrogen fluoride or silicon tetrafluoride. Inasmuch as the purity of the sodium fluosilicate used for one set was not known, the absolute values of the titers are not comparable for the two sets of mixtures, but the titers within each set are comparable among themselves. Of each set, the first three solutions were titrated with hydrochloric acid without being boiled; the next three, after a preliminary titration with hydrochloric acid in the cold, were boiled at such a rate that approximately 10 ml. of water were vaporized in 5 minutes, and then were titrated at once without cooling or further heating; the last three were boiled similarly but before addition of any acid, and then were titrated without cooling or further heating. Each of the resulting acidified mixtures was diluted to approximately 50 ml. and was titrated, after addition of 1 ml. of 0.40 *M* acetic acid, with 0.0500 *N* thorium nitrate in 1.2 *M* acetic acid.

The most important indication discernible from these data is, of course, that the boiling, even when continued for so long as 15 minutes and when the solution is acidified (the indicator, because of escape of carbon dioxide, became pink before boiling began), causes no detectable loss of fluoride. Of most pertinent present interest, however, is the indication that the absolute value of the titer depends to a detectable extent upon the exact pretitration procedure employed. In each set, the average titer was smallest for the solutions that were not boiled at all, and it was largest for the solutions that were boiled before addition of any hydrochloric acid, when they were relatively strongly alkaline. This behavior, which at first appears anomalous, is readily understood from a consideration of the relative pH values of the solutions, as indicated by the hydrochloric acid titration data. The unboiled solutions contained least hydrochloric acid, for carbon dioxide was not expelled; consequently, they had the highest final pH and correspondingly required the smallest titer. The solutions that were boiled before addition of any hydrochloric acid contained practically as much hydrochloric acid as those boiled after a preliminary titration in the cold and, in addition, retained much of the original content of carbon dioxide: consequently, these solutions had the lowest final pH and correspondingly required the largest titer.

From Figure 2, it appears that the thorium nitrate titer is less sensitive to slight pH changes in this method than in that using the chloroacetate buffer, especially for small amounts of fluoride.

CORRECTING FOR INTERFERING FACTORS

Correcting for significant interfering factors can be simply effected in view of the following considerations:

Ideally, or in the absence of interfering factors, the data from the hydrochloric acid titration of a solution obtained by absorbing in *V* ml. of 0.0500 *N* sodium carbonate the acidic combustion products from an analytical sample should satisfy the following equation, in which capital letters indicate quantities directly measured.

$$A + f + s = V$$

in which A = ml. of 0.0500 *N* hydrochloric acid required
f = ml. of 0.0500 *N* hydrofluoric acid equivalent to the fluorine in the sample burned
and s = ml. of 0.0500 *N* sulfuric acid equivalent to the sulfur in the sample burned

However, this equation would be correct only if the final mixture were somehow separated into several solutions, each containing only one salt and having the pH of the equivalence point of this salt, for it is impossible to select one particular pH as indicating a stoichiometrically valid composite equivalence point for all obtainable mixtures of the sodium salts of carbonic, hydrofluoric, sulfuric, and hydrochloric acids. Conversely, in practice, in which one pH must be selected, the hydrochloric acid titration necessarily is not generally a neutralization in the strict sense of yielding a solution reproducible by dissolving in water the appropriate salts.

The situation can be readily improved. Carbonic acid can be eliminated by boiling. Sodium sulfate and sodium chloride, being salts of strong acids, have substantially identical equivalence points, which can be satisfactorily indicated by sodium alizarin sulfonate. Each of the three terms on the left side of the equation can be corrected for interfering factors or can be expressed in terms of the analytical data and readily determinable constants.

Correcting for Buffer Action of Sodium Fluoride. Because the buffer action of sodium fluoride causes A to be too large, A should be decreased by a small volume that is proportional to the amount of fluoride, or to the thorium nitrate equivalent to the fluoride. Thus, A should be corrected to $A - pT$, in which T is the volume, minus the titration blank, of 0.0500 *N* thorium nitrate required to titrate the fluoride, and p is an experimentally determinable proportionality constant.

Correcting for Interference by Sulfate. In the absence of any interference, $f = T$. Accordingly, when fluoride is absent, $T = 0$; but, in the presence of the interference by sulfate, T is a small volume, v, that is obviously proportional to the amount of sulfate. That is, $v = qs$, in which q is an experimentally determinable constant. However, when fluoride is present, v is inadequate as a correction for the interference by sulfate, for this interference is increased in proportion to the amount of fluoride, or to the thorium nitrate required—that is, the full correction is $c = v(1 + kT)$, in which k is an experimentally determinable constant. Hence, $f = T - c$, and $s = v/q = c/q(1 + kT)$.

Rewriting the left side of the equation for the hydrochloric acid titration with the corrected or re-expressed terms, and solving for the correction for interference by sulfate, gives

$$c = q(1 + kT)(V - A + pT - T)/[1 - q(1 + kT)]$$

CORRECTED FLUORINE AND SULFUR CONTENTS

The corrected volume of 0.0500 *N* thorium nitrate is

$$T - c = T - q(1 + kT)(V - A + pT - T)/[1 - q(1 + kT)]$$

The fluorine content in per cent by weight is

$$F = 0.095(T - c)/W$$

in which W is the weight of the sample burned in grams.

Except for correcting T, A is not needed for the determination of F. But A is of prime importance when sulfur is determined as well as fluorine. Ideally, in the absence of any interfering factor, the sulfur content in per cent by weight would be

$$S = 0.08(V - A)/W - 0.842F$$

When A is corrected, as before, for the buffer action of sodium fluoride, the sulfur content is

$$S = 0.08(V - A + pT)/W - 0.842F$$

In the present method, the absorbent volume, V, of 0.0500 N sodium carbonate, is preferably 10.00 ml. From the data of Solutions 8 and 9, Table I, for the excess of hydrochloric acid required because of the buffer action of sodium fluoride, the value of p averages 0.05 ml. of 0.05 N hydrochloric acid for each milliliter of 0.05 N thorium nitrate required. From the data of Solution 17, Table II, 5 ml. of 0.05 N sulfuric acid increase the titration blank (Solution 1, Table I) by v = 0.020 ml., so that q is 0.004 ml. of 0.05 N thorium nitrate for each milliliter of 0.05 N sulfuric acid. From the data of Solution 16, Table II, in comparison with those of Solution 7, Table I, 5 ml. of 0.05 N sulfuric acid increase the thorium nitrate titer for 5 ml. of 0.05 N sodium fluoride by c = 0.63 ml., so that $k = (c - v)/vT = (0.63 - 0.02)/(0.02 \times 5.63) = 5.4$ for each milliliter of 0.05 N thorium nitrate required. Inasmuch as the function of these quantities is merely corrective, evaluation to one or at most two significant figures is adequate.

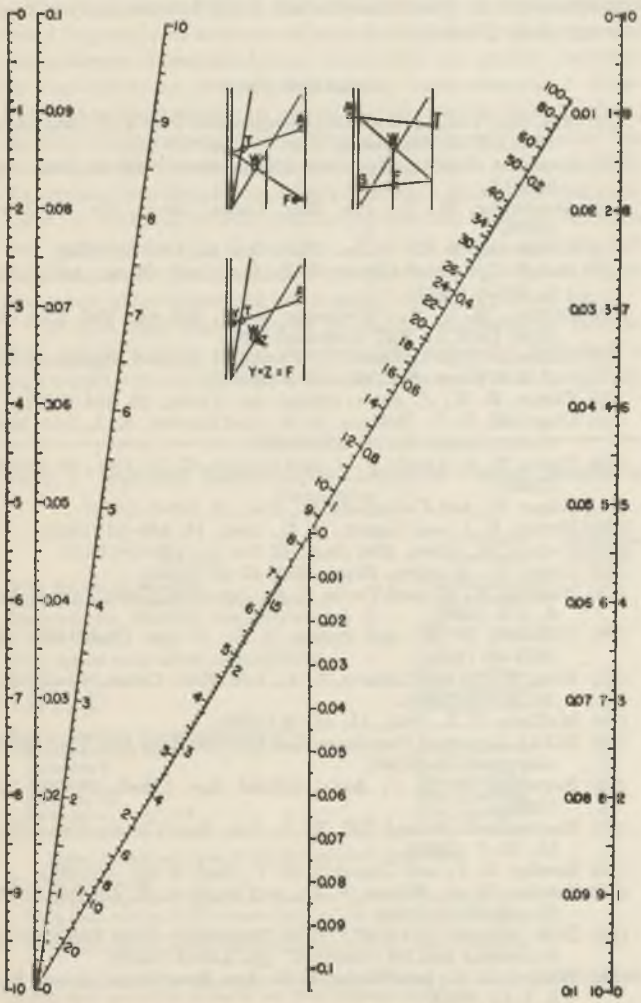

Figure 3. Nomograph for Determination of Fluorine and Sulfur

When these values are used, the equations for fluorine and sulfur contents become

$$F = 0.095[T - (1 + 5.4T)(10.00 - A - 0.95T)/(249 - 5.4T)]/W$$

and $$S = 0.08(10.00 - A + 0.05T)/W - 0.842F$$

These equations, which require only the analytical data, are most easily used in the form of nomographs, such as those combined in Figure 3, to conserve space, into a composite nomograph having the minimum number of lines and scales.

In view of the indication, by the data in Table II for solutions equivalent to an absorbent of 20 ml. of 0.05 N sodium carbonate, that the relationship between c and T departs from rectilinearity for exceedingly large amounts of fluoride or sulfate, W preferably should be so selected that the aggregate of fluorine and sulfur is equivalent to less than 10 ml. of the absorbent, even when V is more than this volume.

DETERMINATION OF OTHER HALOGENS

When sulfur is absent, the acidimetric part of this method is applicable to the determination of a halogen other than fluorine, provided that only one such halogen is present. The equation for the content of such halogen differs from that for sulfur in only the numerical coefficients. For example, for chlorine the content in weight per cent is

$$Cl = 0.1773(V - A + 0.05T)/W - 1.866F$$

Inasmuch as the value thus obtained is subject to the experimental errors of both the acidimetric determination and the fluoride determination, the accuracy cannot be expected to equal that of a method specific for such halogen. Because c = 0 when sulfur is absent, the equation for fluorine content simplifies to

$$F = 0.095T/W$$

DETERMINATION OF ORGANIC FLUORINE AND ORGANIC SULFUR

Apparatus. In the fluorine analysis of a combustible material, such as a liquid hydrocarbon, a lamp assembly incorporating the absorption apparatus illustrated in Figure 1 is used. For gaseous samples the wick-type lamp (*11*, *23*) is replaced by a simple glass burner (*19*); for liquefied gas-and-liquid samples, a glass tube containing a wick is satisfactory. For involatile or difficully combustible samples, the lamp assembly may be replaced by a high-pressure combustion bomb in which the absorbent is placed and in which 0.2 to 1 gram of the sample is burned in the customary manner (*2*); but relatively better recovery of fluorine appears to be obtained by dissolving the sample in isooctane, and burning in a lamp assembly. In addition to the lamp assembly, which, for routine analyses, is in a bank of about six assemblies, a 125-ml. Erlenmeyer flask, a 10-ml. buret, a 5- or 10-ml. microburet graduated in 0.02 ml., and some 1- and 10-ml. pipets are used.

Reagents. For plant-control work, each of the 0.0500 N solutions of sodium carbonate and hydrochloric acid is conveniently prepared without standardization by diluting a commercial 1/10-equivalent preparation to 2000 ml. in a volumetric flask; for precise work, the solutions should be standardized. The indicator is prepared by dissolving 0.25 gram of sodium alizarin sulfonate in water and diluting to 1000 ml. The 0.40 M acetic acid is prepared by diluting 23 ml. (24 grams) of glacial acetic acid to 1000 ml. The 0.0500 N thorium nitrate in 1.2 M acetic acid is prepared by dissolving 13.81 grams of C.P. thorium nitrate tetrahydrate in water, adding 138 ml. (144 grams) of glacial acetic acid, and diluting to 2000 ml. in a volumetric flask; experience indicates that this solution can serve as a primary standard, but if prepared from the dodecahydrate (17.41 grams) it must be standardized against 0.0500 N sodium fluoride, which is prepared by dissolving 2.100 grams of C.P. sodium fluoride, previously dried at about 115° C. for an hour, in enough water to make 1000 ml. Standardization as to acid content of the two solutions containing acetic acid is not necessary.

Color Standards. For the color standards, two stock solutions are prepared: cobalt nitrate, containing 10.0 grams of the C.P. hexahydrate per liter; and sodium chromate, containing 0.125 gram of the C.P. tetrahydrate (this particular hydrate must be used) per liter. The color standard for the hydrochloric acid titration is made by mixing in a 125-ml. Erlenmeyer flask 6 ml. of the cobalt solution, 20 ml. of the chromate solution, and 24 ml. of water. The color standard for the thorium nitrate titration is

Table VI. Typical Duplicate Determinations of Fluorine and Sulfur in Synthetic Mixtures

Hydrocarbon in Mixture	Sample Burned	0.0500 *N* HCl	0.0500 *N* $Th(NO_3)_4$[a]	Fluorine Present	Fluorine Found	Sulfur Present	Sulfur Found
	Grams	*Ml.*	*Ml.*	%	%	%	%
Isooctane	4.33	9.88	0.015	0.0000	0.0000	0.0011	0.002
	3.49	9.97	0.015	0.0000	0.0000	0.0011	0.001
n-Heptane	3.86	9.92	0.015	0.0000	0.0000	0.0021	0.002
	4.27	9.78	0.015	0.0000	0.0000	0.0021	0.004
	3.98	9.87	0.035	0.0005	0.0005	0.0021	0.002
	4.31	9.74	0.040	0.0005	0.0005	0.0021	0.003
	4.91	9.65	0.260	0.0050	0.0047	0.0021	0.002
	4.58	9.51	0.245	0.0050	0.0047	0.0021	0.005
Isooctane	4.84	7.48	2.58	0.0507	0.0502	0.0011	0.002
	4.56	7.55	2.44	0.0507	0.0503	0.0011	0.003
	4.45	1.07	9.31	0.2004	0.198	0.0011	0.002
	3.84	2.25	8.06	0.2004	0.197	0.0011	0.004
	4.96	9.25	0.020	0.0000	0.0000	0.0121	0.012
	4.58	9.20	0.020	0.0000	0.0000	0.0121	0.014
	4.57	4.04	0.045	0.0000	0.0000	0.1113	0.104
	4.45	3.90	0.030	0.0000	0.0000	0.1113	0.110
	4.23	6.84	0.290	0.0050	0.0055	0.0563	0.055
	4.07	6.93	0.285	0.0050	0.0056	0.0563	0.056
	4.75	4.33	2.82	0.0503	0.0520	0.0561	0.054
	4.63	4.37	2.76	0.0503	0.0522	0.0561	0.056
	4.16	0.23	5.03	0.1004	0.1001	0.1110	0.108
	4.28	0.17	5.18	0.1004	0.1004	0.1110	0.104
n-Heptane	4.53	5.01	2.58	0.0537	0.0538	0.1004[b]	0.100[b]
	4.78	4.68	2.71	0.0537	0.0536	0.1004[b]	0.102[b]

[a] In 1.2 *M* acetic acid. [b] Chlorine.

made similarly from 10 ml. of the cobalt solution, 10 ml. of the chromate solution, and 30 ml. of water; in case of doubt as to the proper color, which is sensitive to changes in pH, it is advisable to compare the color with that of a fresh solution duplicating one of those listed in Table I and to adjust the proportions of the stock solutions until the proper color is obtained. If the flask is stoppered, each color standard keeps indefinitely.

PROCEDURE. A portion of the analytical sample, usually from 3 to 10 grams, is burned; the absorbent is 10 ml. of 0.0500 *N* sodium carbonate. When the fluorine content is known to be excessively high, the sample may be preliminarily mixed in known proportion with a suitable diluent, such as isooctane. Highly carbon-rich materials, such as aromatic hydrocarbons, should be diluted with two volumes of ethyl alcohol, to obviate smoking. A blank determination should be made for the diluent.

After the combustion, the absorbent is transferred to a 125-ml. Erlenmeyer flask. A short-stemmed funnel placed in the flask, and a rubber aspirator bulb attached to a rubber stopper fitting the top of the absorber, are helpful in the transfer. The spray trap and the absorption apparatus are washed with small portions of water, which are added to the flask. To the solution is added with a pipet 1 ml. of the indicator. The solution is boiled to expel carbon dioxide and to reduce the volume, if necessary, to about 40 ml. Then, while hot, the solution is titrated with 0.0500 *N* hydrochloric acid delivered from a 10-ml. buret, until the pink color changes to that of the appropriate color standard. It is boiled again briskly for about 2 minutes and is titrated further with the hydrochloric acid. The total acid required is noted.

After the hydrochloric acid titration, the solution is diluted, if necessary, to 50 ml., and 1 ml. of 0.40 *M* acetic acid is added. Then the solution, which may be still fairly hot, is titrated with 0.0500 *N* thorium nitrate in 1.2 *M* acetic acid, delivered from a microburet, until the color matches the appropriate color standard. The titration mixture should be swirled in the flask during the titration and during the color comparison, especially when a precipitate is present.

CALCULATIONS. The calculations are made as indicated by the miniature examples in Figure 3, using the observed values for hydrochloric acid (*A* ml.), thorium nitrate (*T* ml.), and sample burned (*W* grams). (Precisely, *T* is the difference between the thorium nitrate titer and a blank determined by analysis of a sample known to be free from fluorine and from sulfur; this blank, which includes the so-called titration blank, may be taken to be 0.015 ml. of 0.05 *N* thorium nitrate.) The fluorine content (*F*%) should be read to the fourth decimal place; the sulfur content (*S*%), only to the third decimal place. When the content is "off the scale", it can be determined by using, instead of *W*, the product of *W* and a factor of 10 and correspondingly multiplying the content read by the same factor; also correspondingly, when *S* is being determined, *F* must first be divided by the same factor. When *T* is so small that determining *F* directly from the nomograph is inconvenient, *F* can be alternatively obtained by multiplying together values for *Y* and *Z*, read to one or at most two significant figures, as is indicated in one of the miniature examples.

When the standard solutions differ from 0.0500 *N*, *A* and *T* must first be calculated. That is, if the absorbent is 10 ml. of *n N* sodium carbonate, and the acidimetric titration requires *a* ml. of *h N* hydrochloric acid, $A = 10 - 20(10n - ah)$; if *d* ml. of *t N* thorium nitrate is required, and *b* ml. is the corresponding blank, $T = 20(d - b)t$. Obviously, the thorium nitrate should not differ widely from 0.0500 *N*, inasmuch as it contains also acetic acid for control of the pH.

TYPICAL ANALYTICAL DATA

Typical analytical data obtained by this method are presented in Table VI for duplicate determinations of fluorine and sulfur in various known concentrations in isooctane and *n*-heptane (standards for antiknock testing). The sulfur contents of the original hydrocarbons were found by lamp combustion and determination of sulfate by a highly accurate and specific turbidimetric method. Fluorine was added as Eastman α-fluoronaphthalene; sulfur, as Eastman *n*-heptyl sulfide. In one instance, chlorine and fluorine were added as Eastman *o*-fluorochlorobenzene; in this instance, the sulfur in the original hydrocarbon was ignored.

The data, which were obtained with the single-disk apparatus and without special precautions against loss of salt particles from the under surface of the disk, indicate that the method is sufficiently accurate to warrant expressing the fluorine content, in the range of up to 0.1% by weight, to the fourth decimal place; and the sulfur content, in the same range, to the third decimal place.

When a bank of six lamp assemblies is employed, as in routine analyses, six complete analyses are made by one analyst in approximately 3 hours.

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Detection and Estimation of Steam-Distilled Wood Turpentine in Gum Spirits of Turpentine

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ALTHOUGH the Federal Naval Stores Act provides standards of identity for several kinds of turpentine, there is no standard for mixed turpentine, and the sale of such products in interstate commerce is prohibited by the regulations for enforcement of this statute. However, instances have occurred where steam-distilled wood turpentine was added to gum spirits of turpentine and the resultant mixture sold as pure gum spirits. The need of a reliable method for detecting the presence of steam-distilled wood turpentine, when used as an adulterant in gum spirits, has been recognized for some time.

Benzaldehyde was reported as a constituent of steam-distilled wood turpentine in 1927 by Nelson (*4*). Later Palkin, Chadwick, and Matlack (*5*) isolated it from large quantities (15 kg.) of steam-distilled wood turpentine, using a vacuum fractional distillation procedure, and identified it by means of the semicarbazide derivative melting at 213° C. In another paper, Chadwick and Palkin (*2*) reported the absence of benzaldehyde in gum spirits of turpentine, with negative results also on a single sample each of sulfate wood turpentine and destructively distilled wood turpentine.

Thus it was indicated that the presence of steam-distilled wood turpentine in a suspected sample might be shown by proving the presence of benzaldehyde. Aldehydes are usually identified by conversion to phenylhydrazones or semicarbazones. However, since the quantity of benzaldehyde even in straight steam distilled wood turpentine is extremely small, and the latter has often been used as an adulterant in proportions as low as 10%, the actual quantity of benzaldehyde in such an adulterated sample is far too small to lend itself to any method based on isolation and preparation of a derivative. For this reason and the fact that frequently the quantity of sample available for test is limited, some other procedure was sought for the purpose at hand.

The fact that benzaldehyde is readily oxidizable to benzoic acid, which is more easily determinable, suggested that such a step might serve as the basis for a suitable analytical procedure. The ordinary quantitative methods for determining benzoic acid and benzoates in preserved food were discarded, because here too the methods were not applicable to the minute quantities of benzoic acid which could be obtained from the benzaldehyde in an adulterated turpentine.

The Mohler test for benzoic acid was suggested by O. C. Kenworthy and J. Fitelson, U. S. Food and Drug Administration, Federal Security Agency, as serving the purpose of detecting these minute quantities of benzaldehyde, using the Grossfeld modification (*3*) adapted by the Association of Official Agricultural Chemists (*1*) for determining benzoyl peroxide bleach in flour.

The modified Mohler test consists, briefly, of a nitration of the benzoic acid, which is subsequently reduced and converted to 3,5-diaminobenzoic acid. The ammonium salt of this gives a characteristic red color to the solution in which it is formed. The development of a procedure applicable to turpentine for determining benzaldehyde content embraced the problems of separation of interfering oxidation constituents often present in turpentine, extraction and concentration of any benzaldehyde present, its oxidation to benzoic acid, and the application of the Mohler test to develop the characteristic color reaction.

Table I. Indicated Benzaldehyde Content of Various Samples of Turpentine

Sample	Color Developed	Benzaldehyde, P.P.M.
Gum spirits (5 samples)	Yellow, negative	0
Sulfate wood turpentine (4 samples)	Yellow, negative	0
Destructively distilled wood turpentine (3 samples)	Yellow, negative	0
Gum spirits with added benzaldehyde		
10 p.p.m.	Red, positive	7
20 p.p.m.	Red, positive	14
30 p.p.m.	Red, positive	22
Steam-distilled wood turpentines		
Samples 1, 5, 7, 10	Red, positive	22
Samples 6	Red, positive	30
Samples 2, 3, 8	Red, positive	38
Samples 14	Red, positive	45
Samples 4, 9, 11, 12	Red, positive	52
Samples 13	Red, positive	60
Mean for all samples of steam-distilled turpentine		40
Known mixtures		
90% gum spirits, 10% steam-distilled No. 7[a]	Red, positive	2
80% gum spirits, 20% steam-distilled No. 7	Red, positive	4
90% gum spirits, 10% steam-distilled No. 13	Red, positive	6
80% gum spirits, 20% steam-distilled No. 13	Red, positive	10

[a] Sample 7 was the only one of the low-benzaldehyde turpentines available in sufficient quantity to make up these known mixtures.

EXPERIMENTAL

As a preliminary step in this study, five authentic samples of gum spirits of turpentine, representing the product coming from widely separated areas in the southern turpentine belt, were subjected to the test procedure essentially as described below. In no case was the characteristic red color developed in the last step, showing the absence of benzaldehyde in all the gum spirits. Four samples of sulfate wood turpentine and three of destructively distilled wood turpentine, also from widely separated plants, likewise gave negative results.

In order to confirm the reliability and usefulness of the method, small known amounts of benzaldehyde were added to three of the samples of gum spirits. The characteristic color was now obtained when the turpentines were treated as indicated. A series of color standards was prepared at the same time by treating (nitration, reduction, conversion) in a similar manner small quantities of benzoic acid, in ether solution, up to the equivalent of the amount of the benzaldehyde added to the turpentine. Comparison of the colors obtained in the turpentine solutions with those of the standards indicated in every case a recovery or color development equivalent to approximately 70% of the theoretical amount of benzaldehyde added to the turpentine. The results are shown in Table I.

Fourteen authentic samples of steam-distilled wood turpentine, representing the production of the eight largest producers, were then tested. In every instance the red color was obtained, proving the presence of benzaldehyde in all samples of this type of turpentine. By comparison with the prepared color standards it was indicated that the benzaldehyde content of these samples varied from 22 parts per million to 60 p.p.m. with a mean value of about 40 p.p.m. These results are also shown in Table I.

In order to determine whether the benzaldehyde could be concentrated by means of a simple fractional distillation, a 1000-ml. sample of one of the steam-distilled wood turpentines was distilled through a 30-cm. Vigreux column, and the distillate was collected in four 200-ml. portions, leaving a residue of equal volume in the flask. On testing the fractions and the residue

according to the outlined procedure, it was found that the benzaldehyde content was the same in all four fractions, and practically the same in the residue, the sum of the quantities being substantially equal to the total amount of benzaldehyde originally found in the whole sample. Therefore, the benzaldehyde could not be concentrated by such a fractional distillation procedure.

It was observed that certain constituents extracted from the turpentine along with the benzaldehyde were very difficult to oxidize, and imparted a brownish tone to the color developed in the final stage of the test, which interfered with the comparison of the red color of the test solution with that of the standards. This difficulty was overcome by first subjecting the turpentine to a distillation, reserving the portion distilling below 170° C., thereby recovering at least 90% of the sample for testing. The interfering color bodies are thus removed, permitting a more accurate comparison of the colors and closer estimation of the benzaldehyde content of the sample.

PROCEDURE

On the basis of the foregoing discussion and to eliminate all interfering bodies that might adversely affect the final color reaction, the following procedure was carried out:

Distill the sample of turpentine preferably through a 30-cm. Vigreux column, and reserve the fraction distilling below 170° C.

Extract at least 300 ml. of distillate in a 500-ml. separatory funnel, four times, with 10-ml. portions of 30% sodium bisulfite to convert the benzaldehyde to the water-soluble bisulfite addition salt. Combine the extracts, and remove any dissolved turpentine by washing twice with ether, using 25 ml. each time. (As turpentine interferes with the oxidation of the benzaldehyde, all traces must be removed from the bisulfite extract.) Filter the bisulfite extract into another clean separatory funnel. Add carefully (excessive foaming occurs if much ether is present in the extract) small portions of a saturated solution of sodium carbonate until no further effervescence occurs on subsequent addition of carbonate and the solution is alkaline to litmus. Extract the regenerated benzaldehyde from the neutralized solution with 25 ml. of ether, allowing the mixture to stand until the liquid layers are sharply defined and well separated. Draw off the aqueous solution and reserve. Transfer the ether layer into a clean separatory funnel and wash twice with 25-ml. portions of water.

After drawing off all the water, transfer the ether to a 50-ml. test tube, preferably the Pyrex pour-out type, add 2 ml. of approximately 2 *N* sodium hydroxide and a few drops of hydrogen peroxide (30% Superoxol), stopper the tube, and shake. Suspend a thread in the tube to ensure even boiling, and evaporate gently in a warm water bath to dispel the ether.

Return the reserved aqueous carbonate solution to the separatory funnel in which it was first extracted and repeat the extraction with ether, as before; wash, add the ether extract to the test tube, and again evaporate off the ether completely. Place the tube in an oil bath at 120° C. and add a drop or two of hydrogen peroxide at intervals until the solution is almost if not entirely colorless. A few grains of alundum or white sand, or some asbestos fiber which has been treated by boiling with concentrated sodium hydroxide, then with hydrochloric acid, and finally washed with distilled water, may be added to facilitate breaking up the salt cake during nitration. Add a drop or two of water occasionally if the evaporation is too rapid to permit complete decolorizing action of the hydrogen peroxide. Evaporate to complete dryness and heat in a vacuum oven at 100° C. for 30 minutes. If a vacuum oven is not available, complete the evaporation to absolute dryness in the oil bath at 120° C. and finally at 130° C. in a drying oven for 1 hour. Then transfer the tube to a vacuum desiccator charged with a strong drying agent, such as phosphorus pentoxide. When cool add 0.3 gram of potassium nitrate crystals and 3 ml. of concentrated sulfuric acid. Heat in a boiling water bath for 20 minutes, taking care to get all the solid material in solution by breaking up the salt cake with a stirring rod. The nitration must not exceed 25 minutes. Cool the tube in cold water, add 5 ml. of water, then cautiously add 30 ml. of 15% ammonium hydroxide, keeping the tube cool under tap water during the operation. Add 2 ml. of freshly prepared 6% hydroxylamine hydrochloride solution, mix thoroughly, and place in a water bath at 65° C. (avoid overheating, as excessive heat destroys the color) for 5 to 6 minutes, stirring the contents occasionally with a stirring rod. Filter into a clean similar test tube for color comparison. A red color indicates the presence of benzaldehyde in the sample.

An approximation of the quantity of benzaldehyde present in a sample of turpentine suspected to contain steam-distilled wood turpentine should serve to give a rough idea as to the extent of such adulteration. To make such an approximation it is necessary to prepare a series of color standards representing definite quantities of benzoic acid in ether solution.

Dissolve 104 mg. of C.P. benzoic acid in 100 ml. of ether and proceed as follows: Pipet 0.2 ml., 0.4 ml., etc., to 2.0 ml. of this solution into similar test tubes. These quantities represent approximately 1 p.p.m., 2 p.p.m., etc., to 10 p.p.m., respectively, of benzaldehyde for 300 ml. of sample. Add 2 ml. of 2 *N* sodium hydroxide, a few drops of hydrogen peroxide, and proceed as outlined in the method, beginning with the evaporation of the ether. Compare the test solution with the nearest color standard.

On a basis of 70% recovery of added benzaldehyde, as previously indicated, the benzaldehyde content of a turpentine, in p.p.m. (mg. of C_6H_5CHO per kg. of sample), is as follows:

$$\text{P.p.m.} = W \times \frac{1000}{SXV} \times \frac{\text{moles of } C_6H_5CHO}{\text{moles of } C_6H_5COOH} \times \frac{100\%}{70\%}$$

where W = weight in mg. of benzoic acid in the standard matching the test solution
S = specific gravity of sample
V = volume of sample

Since the specific gravity of turpentine at room temperature ranges from 0.852 to 0.867 with an average of 0.860, for 300 ml. of sample the equation may be stated as follows:

$$\text{P.p.m.} = W \times \frac{1000}{0.860 \times 300} \times \frac{106}{122} \times \frac{100}{70} = W \times 4.81$$

A set of Lovibond color glasses may be used in place of the laboriously prepared series of benzoic acid color standards, for estimating the benzaldehyde content of a sample. The red glasses required with the corresponding benzaldehyde content of the color standards are shown in Table II. The comparisons are for a 15-cm. depth of standard solutions measured in 50-ml. standard Nessler tubes.

Table II. Lovibond Standards for Benzaldehyde

Standard No.	Benzoic Acid Solution	Benzaldehyde Equivalent	Lovibond Glass	
			Red	Yellow
	Ml.	*P.p.m.*		
1	0.2	1	3.5	2.1
2	0.4	2	9.5	4.8
3	0.6	3	14.0	5.6
4	0.8	4	18.0	4.8
5	1.0	5	21.0	5.6
6	1.2	6	24.0	2.5
7	1.4	7	27.0	3.6
8	1.6	8	30.0	2.5
9	1.8	9	33.0	4.8
10	2.0	10	36.0	2.5

It was necessary to use a yellow Lovibond glass with the red glass to obtain an approximate color match. The variation in the yellow color is due to the oxides of nitrogen released when the ammonia is added, giving rise to a yellow color in the mixture which cannot be controlled. However, since the yellow color has no bearing on the quantity of benzaldehyde indicated by the intensity of the red color of the solution, for ordinary purposes the analyst is free to use any yellow needed to obtain a match without affecting the conclusions to be drawn from the value of the red glass used. An alternative would be to use a single yellow glass (either a No. 3 or No. 4) for all red-yellow combinations, this being close to the average of the yellow glass values listed in the table.

Mixtures of gum spirits of turpentine, previously tested and found to be free of benzaldehyde, and two steam-distilled wood turpentines of determined benzaldehyde content were prepared for examination and then analyzed for benzaldehyde by the proposed method. From these data, on the basis of the mean benzaldehyde content of steam-distilled wood turpentine, it is reasonable to assume that any sample of gum turpentine showing so much as 4 p.p.m. of benzaldehyde by this method contains at least 10% of steam-distilled wood turpentine.

The utmost precision must be exercised in order to obtain reliable results. It is always advisable to prepare a few of the color standards along with the test to ensure that the procedure has been properly followed and each reaction carried to completion. Vigorous shaking of the mixtures during extraction should be avoided, as emulsification of the ether extracts precludes a good separation and interferes with the reactions in the successive steps of the procedure. Other precautions to be taken are the evaporation to complete dryness of the ether extract for the nitration and avoiding overheating of the hydroxylamine hydrochloride mixture.

SUMMARY

There have been instances where steam-distilled wood turpentine has been used to adulterate gum spirits of turpentine. Of the four kinds of turpentine—gum spirits of turpentine, steam-distilled wood turpentine, sulfate wood turpentine, and destructively distilled wood turpentine—benzaldehyde has been found only in steam-distilled wood turpentine.

A method is proposed for determining the presence of benzaldehyde in a sample of turpentine, by means of a modification of Mohler's test for benzoic acid. Its detection is therefore considered evidence of the presence of steam-distilled wood turpentine.

From the quantjty of benzaldehyde indicated by the procedure a basis for roughly approximating the extent of adulteration with steam-distilled wood turpentine is given.

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Analysis of Silver Plating Solutions

A Simple Electrometric Method

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Methods for the electrometric determination of free cyanide and argenticyanide in silver plating baths are described. Both ions can be determined by the same run of the buret with silver nitrate solution. The end points are detected by null-point readings on a galvanometer. The method requires inexpensive equipment and is very rapid and easy to carry out. The effect of other ions often found in electroplating solutions has also been investigated.

IN A previous paper (*2*) it was shown that an estimate of free cyanide and argenticyanide in a silver plating solution could be obtained by titration with silver nitrate solution. The free cyanide was estimated by the well-known Liebig method, in which the solution is titrated to the first sign of turbidity owing to the formation of silver cyanide after the reaction

$$2KCN + AgNO_3 = KNO_3 + KAg(CN)_2 \qquad (I)$$

is completed.

Further addition of silver nitrate involves the reaction

$$KAg(CN)_2 + AgNO_3 = KNO_3 + Ag_2(CN)_2\downarrow \qquad (II)$$

It has been shown that the end point of this reaction can be detected by the use of potassium chromate as an indicator, provided the solution is buffered with excess of boric acid. In this manner, with an electroplating solution containing potassium cyanide and potassium argenticyanide, the difference between the titration to complete precipitation of silver cyanide and twice the Liebig titration on a similar aliquot is equivalent to the argenticyanide originally in the solution.

Wick (*5*) and Müller and Lauterbach (*3*) investigated the variation of potential of a silver electrode in solutions of alkali cyanide during titration with silver nitrate. It was found that there were two distinct sudden changes in the potential during the titration. The first change occurred at the end of the first reaction (I), and the point of maximum variation of e.m.f. coincided with the appearance of turbidity. The second fluctuation in e.m.f. occurs when the silver cyanide is completely precipitated at the end of the second reaction (II).

The silver-ion concentration at this point is increasing very rapidly, owing to complete precipitation of the silver cyanide with consequent increase in the e.m.f. of the silver electrode. The second point of inflection took place when exactly twice as much silver nitrate as for the first point of inflection had been added. Thus the e.m.f.–silver nitrate curve represents accurately the two stages of the reaction of precipitation of silver cyanide.

Read and Read (*4*) have also described an electrometric method of estimating argenticyanide in conjunction with Liebig's titration. In this method the electrodes are of platinum and tungsten, respectively. Towards the end point of the second stage of the reaction, the potential of this system (indicated by a vacuum tube voltmeter) shows a slight rise, followed by a sudden drop at the end point. No suggestions are made in this paper as to the theory of the action of this method and why it is sensitive to a change in silver-ion concentration. The same authors describe a method of detecting the end point of the second reaction by the use of diphenyl carbazone as an internal indicator. A color change from violet to a dirty blue occurs at the end point.

Müller and Lauterbach have studied the effect of the presence of halides on the electrometric titration curve of cyanide, and have shown that, as each halide is precipitated in turn according to its solubility, a marked discontinuity occurs in the curve at points which are equivalent to the amount of halide present. In this manner halogens can be determined electrometrically in the presence of cyanide.

Cavanagh (*1*) has described a simple absolute method of potentiometric titration in which the e.m.f. at the end point of the titration is counterbalanced by an equal and opposite e.m.f. The end point of the reaction is then indicated by a null reading on a galvanometer in series in the circuit. In the reactions to which this is applicable there is a rapid change in e.m.f. at the end point and a very sensitive detection is possible with a moderately sensitive galvanometer. Only an approximate adjustment of the counterbalancing potential is required in this titration, since at the end point the addition of 0.05 ml. of 0.1 *N* solution often causes a change of 50 to 100 millivolts in the e.m.f.

Cavanagh used this method for the titration of halides with silver nitrate. He ensures zero e.m.f. at the end point by having a quinhydrone electrode as his reference electrode and a silver–silver halide electrode as the reversible variable electrode. The pH of the solution is then adjusted by addition of nitric acid of known strength until the potential of the quinhydrone electrode is known to be equal and opposite to that of the silver halide electrode at the end point.

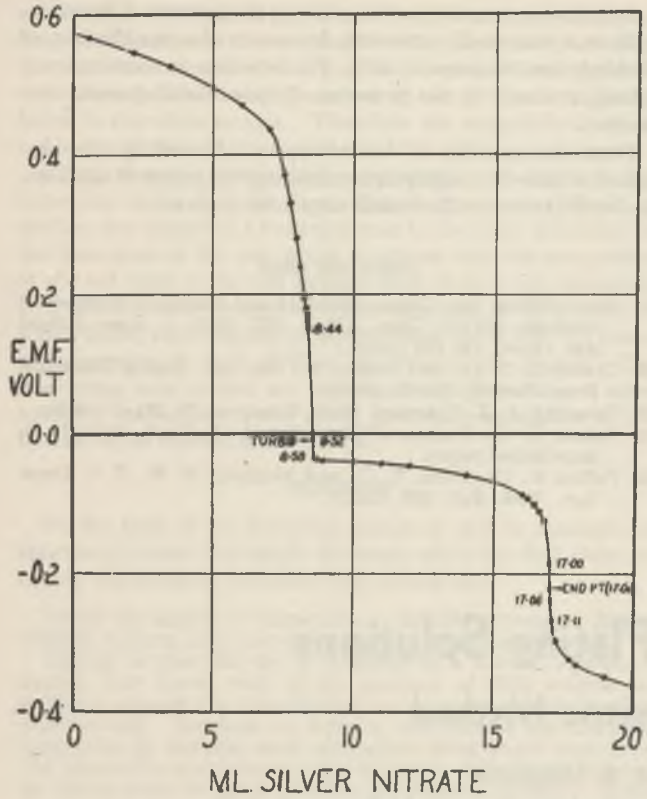

Figure 1

In the case of the chloride titration, the e.m.f. of the cell is given by:

$$E = 0.474 + 0.0575 \log_{10}(C_{H^+} \times C_{Cl^-})$$

C_{H^+} and C_{Cl^-} are the concentrations of hydrogen and chloride ion, respectively.

At the end point of the reaction C_{Cl^-} is equal to the square root of the solubility product of silver chloride,

$$C_{Cl^-} = 0.97 \times 10^{-5}$$

From this it may be calculated that, for E to be zero at this point, the value of C_{H^+} should be about 0.00055 N. This adjustment can be made with sufficient accuracy by addition of the necessary amount of standard nitric acid from a graduated pipet. The cell is then simply connected in series with a tapping key, suitable resistances, and a galvanometer and the titration is continued until the galvanometer passes zero deflection.

The object of the present investigation was to endeavor to apply the variation of the potential of the silver electrode to a simple and rapid method for determining the cyanide and argenticyanide concentration of plating solutions. As the method is intended for routine control with limited facilities, speed and simplicity of operation are the essential requirements. An accuracy of ±1% is sufficient in this estimation.

EXPERIMENTAL

Titration of Pure Cyanide Solutions. At first experiments were carried out to determine whether Cavanagh's method could be applied to the precipitation of silver cyanide by silver nitrate, and, if so, what concentration of hydrogen ion gives the correct potential of the quinhydrone electrode. The adjustment of hydrogen-ion concentration is necessarily restricted by the instability of cyanides which occurs even in weakly acid solutions. It so happened, however, that a saturated solution of boric acid (pH = 5.0) gave the correct hydrogen-ion concentration. Thus the solution was adjusted in a manner similar to the titration with chromate indicator (*2*). Pure 0.2 N potassium cyanide was titrated with 0.2 N silver nitrate first by the Liebig method, and second by the procedure outlined below.

A 20-ml. aliquot was diluted to about 40 ml. and then the silver nitrate solution was added until there was almost sufficient to precipitate the cyanide. At this stage, excess boric acid and about 0.5 gram of quinhydrone were added and stirred well. A silver and a bright platinum electrode were each inserted in the solution and connected via a tapping key and variable rheostat to a galvanometer. The addition of silver nitrate was then continued slowly until the addition of one drop caused a change in deflection of the galvanometer from the $+ve$ to $-ve$ direction.

The Liebig titration is a reliable method, and by it one can obtain the potassium cyanide concentration of the solution relative to the silver nitrate. If the electrometric end point is correct, then it should give a titer exactly twice that of the Liebig method. The results obtained are given in Table I.

Table I. Titers

(20-ml. aliquots of KCN)

Titers by Liebig Method	Titers by Electrometric Method
Ml.	*Ml.*
9.51	18.87
9.47	18.96
	18.99
	18.94
Av. 9.49	18.94

Ratio of electrometric to Liebig titer = 1.997.

A measurement of the e.m.f. of the silver electrode against the saturated calomel electrode showed a value of 0.42 volt as the equivalence point. The e.m.f. of a quinhydrone electrode it 0.41 volt at pH 5.0. Thus, from a theoretical basis, the e.m.f. of the combination should be zero at the end point of the reaction.

This method, if applied to the analysis of electroplating solutions, would require two titrations (the Liebig titration for free cyanide and the electrometric for argenticyanide). It was felt that it would be an advantage to be able to do the two estimations on the same run of the buret. The Liebig and electrometric method described above could not be combined, since the former requires dilution to about 600 ml. in the presence of carbonate ion, which is nearly always present in silver plating solutions, while the latter requires the minimum possible volume of solution.

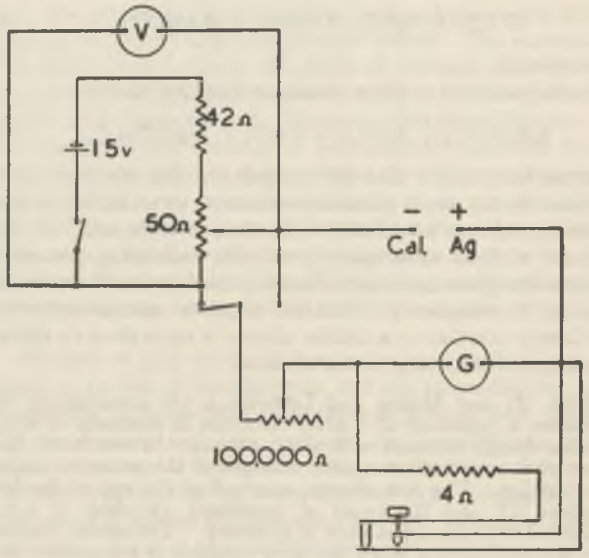

Figure 2

Figure 1 shows the titration curve of 0.2 *N* potassium cyanide solution with 0.2 *N* silver nitrate, using a silver electrode with a saturated calomel electrode as reference electrode. The calomel electrode was connected to the solution via a 25% ammonium nitrate bridge. The ammonium nitrate bridge was used to prevent the solution becoming contaminated with chloride ions. The cell set up was thus:

$$\text{——Ag}\,|\,\underset{\text{(titrated solution)}}{\text{Ag}^+}\,:25\%\ \text{NH}_4\text{NO}_3:\text{Satd. KCl}:\text{Hg}_2\text{Cl}_2\,|\text{Hg——}$$

A 20-ml. aliquot of potassium cyanide was taken and diluted to 600 ml. for this titration. It is seen that there is a very large drop in e.m.f. at the first end point, and the e.m.f. passes zero at the point of appearance of turbidity (8.52 ml.). The second point of inflection of the curve corresponds to complete precipitation of silver cyanide and the volume now is exactly twice the first (17.04 ml.). The sensitivity is such, at the end point, that one drop of silver nitrate causes a change of 50 millivolts in e.m.f. These results were obtained consistently under the same conditions, and variation of the amount of dilution between 200 and 600 ml. had practically no effect on the titers or the e.m.f. at the end points. The values of the e.m.f. at the end points were zero and −0.21 to −0.22 volt, respectively (the calomel electrode was taken as +*ve* at the beginning of the titration).

Using the equation

$$E = 0.80 + 0.058 \log_{10}(C_{A_g^+})$$

where $C_{A_g^+}$ = concentration of silver ions

it can be calculated that the e.m.f. at the equivalence point (where $C_{A_g^+} = \sqrt{S.P.\ Ag_2(CN)_2} = 1.5 \times 10^{-6}$) should be −0.21 volt against the saturated calomel electrode. This is in close agreement with the observed value of −0.21 to −0.22 volt for the point of inflection of the curve.

The detection of the first end point is a simple matter in this case. One can either use the appearance of turbidity or the zero e.m.f. (null point on galvanometer in series).

For the simple detection of the second end point, a method suggested by Müller and Lauterbach and Cavanagh can be used—i.e., after passing the first end point, an e.m.f. of 0.22 volt is applied in series in the circuit in the opposite direction to the cell e.m.f. The resultant e.m.f. is thus 0 at the second end point, and the titration can be continued until a series galvanometer again shows a zero deflection. The e.m.f. is applied by means of a potentiometer circuit, and the complete circuit is shown in Figure 2. An e.m.f. up to 1.0 volt can be placed in the circuit by adjustment of the potentiometer and its value read on the voltmeter. The potentiometer can be switched out of the circuit if desired, for detecting the first end point. The press button in the galvanometer circuit is designed with its free position in open circuit, a light pressure closes the circuit with a low resistance shunt on the galvanometer, and a heavier pressure removes the shunt, with the circuit still closed. In this manner the first pressure enables one to detect currents which might otherwise ruin the galvanometer if connected directly. The 100,000Ω variable series resistance is used also to protect the galvanometer when relatively large e.m.f.'s are present. Figure 3 shows the layout of the circuit and galvanometer setup used in this work.

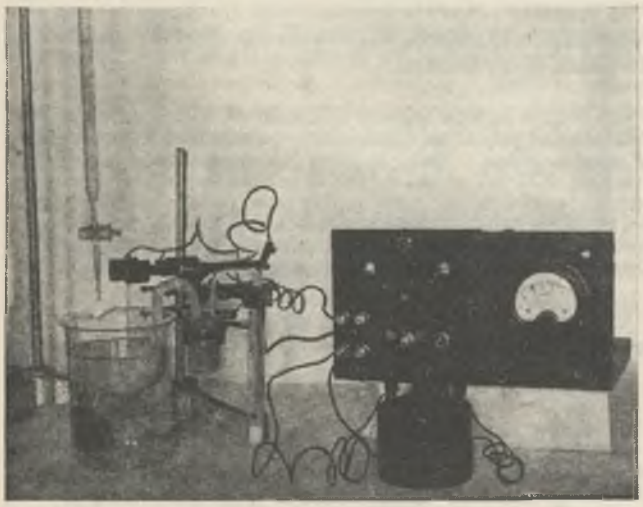

Figure 3

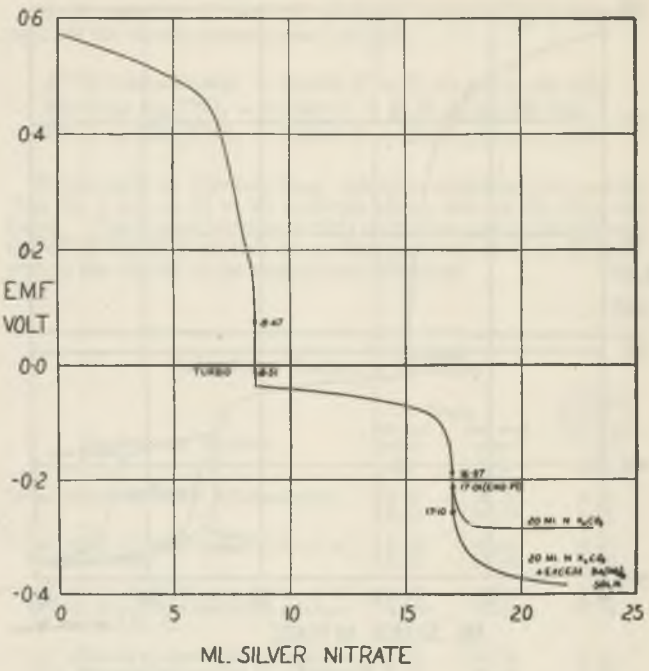

Figure 4

Table II. Titers on Pure Cyanide Solutions

Conditions of Titration	Titers of 0.2 *N* $AgNO_3$: To 1st end point (turbidity) *Ml.*	To 2nd end point (0.22 volt) *Ml.*	Ratio of Titers
20 ml. of 0.2 *N* KCN diluted to 250 ml.	9.43 9.37	18.82 18.70	1.997 1.997
20 ml. of 0.2 *N* KCN diluted to 600 ml.	9.34 9.36	18.70 18.73	2.002 2.001
20 ml. of 0.3 *N* KCN diluted to 600 ml.	15.41 15.43	30.81 30.81	2.000 1.996

In detecting the second end point, the potentiometer is set on 0.22 volt and switched into the circuit. Silver nitrate solution is then added, the circuit being closed after each addition until the deflections start to decrease slowly. The series resistance may then be reduced and the titration continued slowly. At the end point, with the series resistance right out, the addition of one drop of silver nitrate causes a full-scale deflection on one side of the galvanometer to change to a full-scale deflection on the other side.

Table II shows the results of titers carried out on pure cyanide solutions by this method. The titer to the Liebig end point (turbidity) corresponded exactly to the galvanometer null point in all cases. This end point is again used as a standard for comparison of the second end point, as it is impossible to weigh out accurate samples of cyanide. The ratio between first and second end points gives an indication of the accuracy of the second end point.

The method gives reliable and accurate results on pure cyanide solutions. Silver electroplating solutions, however, also contain alkali carbonate added intentionally and sometimes small quantities of other ions introduced during the working of the plant by corrosion of the baths, electrodes, etc., and it is essential that the effect of these ions should be investigated. Chloride ion is a common impurity, usually introduced in the chemicals used for making up the bath. Traces of iron, copper, and other heavy metals are present as complex cyanides. These are usually acquired by corrosion of the plant and objects being plated, etc.

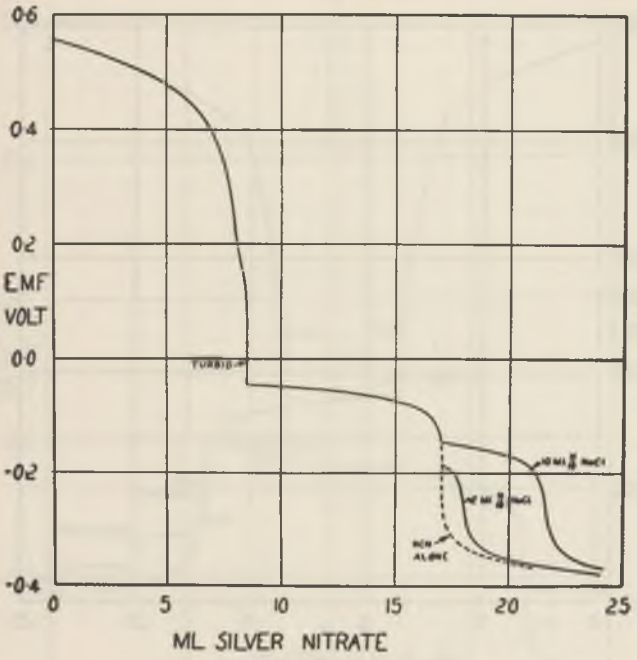

Figure 5

EFFECT OF OTHER IONS ON THE TITRATION. *Carbonate.*

To 20 ml. of 0.2 *N* potassium cyanide were added 20 ml. of *N* potassium carbonate, making the solution 0.5 *N* with respect to carbonate. This is the concentration which is used frequently in electroplating solutions. The titration curve of this solution, when diluted to 600 ml., is shown in Figure 4. (The cyanide is the same solution as used in Figure 1.) It is seen that, owing to the greater solubility of silver carbonate than silver cyanide, the carbonate has no appreciable effect on the titration curve until after all the silver cyanide is precipitated. The light brown silver carbonate can be seen to be precipitating after the end point is passed. The change in e.m.f. is slightly less rapid than in the absence of carbonate, but this is easily overcome by the addition of excess barium nitrate solution, as shown in Figure 4.

From the value of the solubility product of silver carbonate, it can be calculated that the carbonate in this concentration should commence to precipitate silver carbonate when $C_{Ag^+} = 1.34 \times 10^{-5}$. When this concentration of silver ion is reached, the e.m.f. is calculated to be −0.27 volt. There is no sharp point on the titration curve at which carbonate starts to precipitate, but the effect is first observed in the range from −0.23 to −0.28 volt. The dilution of the solution to 600 ml. assists not only the first end point but also the second, in that the lower the concentration of carbonate, the lower the e.m.f. at which silver carbonate precipitates.

On the whole, carbonate has no appreciable effect on both stages of the titration when present in moderate quantities, and even this slight effect can be removed by the addition of excess barium nitrate and dilution of the solution to about 600 ml. If no barium nitrate is added, it is advisable to have the interposed e.m.f. slightly lower—i.e., 0.19 to 0.21 volt.

Chloride. The effect of chloride is slightly more marked than carbonate. Owing to the lower solubility of silver chloride, it commences to precipitate at a higher e m.f. and lower silver concentration.

Figure 5 shows the effect of adding 10 ml. and 2 ml. of 0.1 *N* sodium chloride to the 20-ml. aliquot of potassium cyanide. This is equivalent to concentrations of 0.033 *N* and 0.01 *N* in the electroplating solution, and after dilution to 600 ml. the concentrations of chloride ion are 0.0013 and 0.00033 *N*. At these concentrations the solubility product of silver chloride is exceeded when $C_{Ag^+} = 9.36 \times 10^{-8}$ and 4.68×10^{-7}, respectively. Using the equation for the silver electrode $E = 0.80 + 0.058 \log_{10} C_{Ag^+}$, it can be calculated that the precipitation should commence at e.m.f. of −0.14 and −0.18 volt against the saturated calomel electrode. It is seen from Figure 5 that the precipitation is observed to commence at −0.15 and −0.19 volt. The point of inflection of the curves indicates the complete precipitation of silver chloride and the difference between these end points and the cyanide end point is almost exactly equivalent to the amount of chloride present; 10 ml. of the sodium chloride are equivalent to 4.63 ml. of silver nitrate, and the difference in end points is 4.65 ml. Similarly, with 2 ml. of 0.1 *N* sodium chloride, the difference is 1.00 ml., the theoretical difference being 0.93 ml.

The presence of reasonably small concentrations of chloride ion in the solution should not have any marked effect on the cyanide estimation. If the point at which the silver chloride starts to precipitate is taken as the end point, with 10 ml. of 0.1 *N* sodium chloride present the error involved is only about 0.05 ml. in the titer. If chloride ions can be detected in the solution, either by a potentiometric titration or the recognized chemical methods, it is advisable to use a lower e.m.f. at the end point, say 0.15 volt (according to the amount of chloride ion present). The cyanide estimation would be slightly low, but by setting the potentiometer later to about 0.26 volt the chloride ion concentration can be determined in the same titer.

The circuit as shown in Figure 2 can be used for determining the complete titration curve. To measure any unknown e.m.f. in the cell, it is only necessary to adjust the potentiometer until the galvanometer is undeflected. The potential is then read off the meter.

Hydroxide. Titration curves were determined for the usual amount of cyanide with 10 and 2 ml. of 0.1 *N* potassium hydroxide present. The alkali in these concentrations had practically no effect on the results for the cyanide titration, and silver oxide did not start to precipitate until all the silver cyanide had been thrown down. There was a slight flattening of the curve below the end point, and this appeared to be the only effect of the presence of caustic alkali.

Copper. Two titration curves were made with 2 and 5 ml. of 0.2 *N* cupric sulfate present. Two definite end points were shown, but the rate of change of e.m.f. at the end points was much slower than usual. The presence of copper also caused a lowering of both titers by an equal amount, as shown in Table III.

The reduction of the first titer can be explained quantitatively by the formation of a complex cuprocyanide. On addition of the copper sulfate to the cyanide solution, a yellow-brown precipitate of cupric cyanide is formed instantaneously. The precipitate, however, dissolves immediately in the excess potassium cyanide. The reaction is probably

$$2KCN + CuSO_4 = Cu(CN)_2 + K_2SO_4$$
$$Cu(CN)_2 + KCN = KCu(CN)_2$$

It is probable that the complex loses cyanogen, forming the cuprocyanide, $KCu(CN)_2$, but this does not affect the quantitative discussion of the reaction.

The cupric sulfate solution is 0.2058 *N*, and it is seen that 3/2 moles of potassium cyanide are equivalent to one equivalent of cupric sulfate. Thus, to form the potassium cuprocyanide complex, 9.17 ml. of the 0.1683 *N* potassium cyanide would be required with 5 ml. of cupric sulfate present and 3.67 ml. with 2 ml. of cupric sulfate. This would leave the amount of potassium cyanide in 10.83 and 16.33 ml. unchanged. To the first end point, these would be equivalent to 4.62 and 6.96 ml. of silver nitrate,

Table III. Effect of Copper on Titration

0.2 *N* $CuSO_4$ Present, Ml.	Titer to 1st End Point	Titer to 2nd End Point	Difference of 1st and 2nd End Points
0	8.52	17.04	8.52
2	6.94	15.50	8.56
5	4.40	13.02	8.62

respectively. The actual titers obtained are 4.40 and 6.94 ml. (Table III). Furthermore, titration of 10 ml. of 0.3 *N* potassium cyanide solution with 0.1 *N* cupric sulfate requires exactly 20 ml. of cupric sulfate to the first appearance of turbidity. This corresponds exactly to the formation of the potassium cuprocyanide complex by the equations given above. It is clear that the addition of copper will reduce the cyanide content of the solution, but it does not affect the actual determination of the free cyanide remaining.

The effect of copper on the second end point is more difficult to explain. It seems that a fairly complicated series of reactions occurs. At first a white precipitate, which contains copper, is formed. After the fluctuation in e.m.f., the precipitate starts to go brown on further addition of silver nitrate. This is due to a reaction of the precipitate and silver nitrate, for it does not occur if the precipitate is removed by filtration at the end point. Both the precipitate and supernatant liquid at the point of maximum fluctuation of e.m.f. are shown to contain copper. It seems that the only reaction which could possibly fit the experimental data is one in which the cuprocyanide complex reacts with silver nitrate during the second stage of the titration in the following manner:

$$2KCu(CN)_2 + 3AgNO_3 = 2KNO_3 + Ag_2(CN)_2\downarrow + AgCu(CN)_2\downarrow + CuNO_3$$

Assuming this reaction, the difference between first and second end points would be 8.3 ml. (actually 8.62) when 5 ml. of 0.2 *N* cupric sulfate are present. There is no certainty that this is the correct reaction involved, but of all possible simple reactions it gives values nearest the observed results. The true reaction is probably more complicated. However, the presence of appreciable quantities of copper will have a marked effect on the second end point in the titration. Small amounts of copper present, however, could probably be neglected.

Mercury. The presence of mercuric salts has much the same effect on the titers as copper salts. The effect of mercury is not considered very important, as it would be very uncommon in electroplating solutions.

Zinc. The presence of 5 ml. of 0.2 *N* zinc sulfate had no visible effect on the titration curve.

Ferrocyanide. The presence of ferrocyanide had a very slight effect on the turbidity end point. The titers were 0.05 to 0.10 ml. too high if the appearance of turbidity were taken as the end point. Taking the zero e.m.f. as end point, however, gave the correct result. The second end point was increased in an amount equivalent to the amount of ferrocyanide present assuming $Ag_4Fe(CN)_6$ is formed. Apparently the $Ag_2(CN)_2$ and $Ag_4Fe(CN)_6$ precipitate together, as there is no break in the curve after the turbidity commences. If appreciable quantities of iron are present in the solution, it usually occurs as ferrocyanide, and in order to obtain an accurate silver estimation it will be necessary to know the amount of ferrocyanide ion present and make the necessary deduction from the titer. There are methods described in the literature (*5*) for the estimation of iron in such solutions.

Titration of Solutions, Using the Galvanometer Null Point as Indicator. As a final test of the method, several solutions were titrated, using the method described previously with series galvanometer and interposed e.m.f. at the second end point. The results are shown in Table IV.

Calculation of Result on Unknown Electroplating Solution in Table IV.

Free cyanide in 10 ml. is equivalent to 12.72 ml. of 0.1911 *N* silver nitrate.

The volume of silver nitrate equivalent to the argenticyanide in the solution is equal to the titer to the second end point (35.35 ml.) less twice the free cyanide titer (2 × 12.72 ml.). Therefore argenticyanide is equivalent to 9.91 ml. of 0.1911 *N* silver nitrate.

As the solution is made up of silver cyanide and potassium cyanide the results are expressed as such:

KCN (uncombined) = 0.2432 *N* = 31.65 grams per liter
Silver as $Ag_2(CN)_2$ = 0.1893 *N* = 25.35 grams per liter
Silver as $KAg(CN)_2$ = 0.1893 *N* = 37.67 grams per liter

Occasionally in titrating these unknown solutions it is noticed that the e.m.f. is 10 or 20 millivolt above zero at the first end point. This is possibly due to high carbonate concentration, and the effect can be overcome by putting an e.m.f. of 10 to 20 millivolt in the circuit in the appropriate direction.

Table IV. Titration of Solutions

Conditions of Titration	Titers: 1st end point	Titers: 2nd end point	Applied E.M.F. at 2nd End Point
	Ml.	*Ml.*	*Volt*
20 ml. aliquots of 0.3 *N* KCN solutions	15.41	30.81	0.23
	15.43	30.81	0.23
20 ml. of 0.3 *N* KCN, plus 20 ml. of *N* K_2CO_3 solution	15.45	30.85	0.19
	15.45	30.85	0.19
20 ml. of 0.3 *N* KCN, plus 20 ml. of *N* K_2CO_3, plus excess $Ba(NO_3)_2$ solution (40 ml. of 0.65 *N*)	15.47	30.90	0.23
	16.08[a]	32.20	0.23
10-ml. aliquots of silver plating solution after intermittent use for 15 months; $CO_3^=$ all precipitated by excess barium nitrate	12.70	35.37	0.22
	12.72	35.35	0.22
	12.72	35.35	0.22
Av.	12.72	35.35	

[a] New silver nitrate solution.

CONCLUSIONS

The estimation of free cyanide and argenticyanide in a silver plating solution can both be carried out in the one titration, using electrometric methods to detect the Liebig end point and the point of complete precipitation of silver cyanide. It has been shown that zinc, chloride, hydroxide, and carbonate show no appreciable interference with the method. The presence of copper, iron, and mercury, however, can have quantitative effects on the titration to the second end point. These impurities are normally never present except in very small concentration and do not really militate against the method of analysis.

It is important to note that the presence of chloride can be detected quantitatively by continuing the titration after the cyanide end point. The effect of ferrocyanide—probably the commonest heavy metal impurity—can be shown quantitatively and allowed for if the iron content is known accurately.

The accuracy of the electrometric method is much in excess of that usually required for electroplating solution analysis, and the sensitivity of the end point is much less than one drop (0.03 ml.) of 0.2 *N* silver nitrate.

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Correction—1944 Index

On the second page of the Author Index of the Analytical Edition for 1944, printed in the December issue, the name of Fritz Feigl was omitted from the reference to the article by Fritz Feigl and L. I. Miranda on "Selective Spot Microreaction for Cadmium", page 141.

Determining Traces of Bismuth in Copper by Means of Dithizone

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A method is proposed for the determination of traces of bismuth in copper. No new principles are involved. Bismuth is first collected by hydrated manganese dioxide. Bismuth and lead are then extracted in an alkaline medium of cyanide by solution of dithizone in carbon tetrachloride. Finally bismuth is titrated by the solution of dithizone at pH 3. Since this method requires no special apparatus and takes only 2 to 3 hours to run a single analysis, it is suitable for a control method in a copper refinery.

SEVERAL methods have been proposed for the determination of traces of bismuth in copper (*9*). In brief, bismuth is first separated from large quantities of copper by a collective agent, such as ferric hydroxide (*10*), or hydrated manganese dioxide (*6*, *7*), or an extractive agent such as dithizone (*3*); it is then determined spectrographically (*7*) or colorimetrically (*3*, *6*, *10*). An entirely different method (*2*) consists of the formation of a bismuth mirror when copper millings are heated at 1050° to 1060° C. in a stream of hydrogen.

Both the method involving the bismuth mirror and the spectrographic method require elaborate apparatus not usually available in copper refineries. The extraction of bismuth directly from copper solution in an alkaline medium of cyanide is objectionable in that large quantities of cyanide have to be added to keep the copper ion in complex form, which results in the liberation of much toxic hydrogen cyanide and cyanogen. The colorimetric method (iodobismuthite method) is interfered with by many ions which liberate iodine or form insoluble iodides. Some investigators suggest the use of acid sulfite or stannous chloride solution to reduce the iodine so liberated, but even so the difficulties involved are far from being solved. Thus, a simple and fairly accurate method of determining traces of bismuth in copper is needed for control purposes.

This paper suggests a method using dithizone and incorporating the following principles:

Hydrated manganese dioxide is used as a collector of bismuth (*7*). This effects a rough separation of bismuth from copper, without loss of bismuth.

The precipitate of manganese dioxide is dissolved and the bismuth is extracted from an ammoniacal solution of cyanide with a solution of dithizone in carbon tetrachloride. According to Fischer (*4*), Bi^{+++}, Pb^{++}, Sn^{++}, and Tl^{+} are the possible ions so extracted. Thallium is not likely to be present in ordinary copper. Tin is oxidized during the dissolution of copper. Therefore, lead is the only other element coextracted with bismuth in appreciable amounts.

The dithizonates of lead and bismuth are thrown back from the carbon tetrachloride phase into the water phase by shaking them with dilute acid. Bismuth is the only element titrated out by the solution of dithizone at pH 3 (*1*, *5*, *11*).

PROCEDURE

Dissolve a suitable weight of copper, containing about 10 to 60 micrograms of bismuth, in dilute nitric acid (1 + 1). If the content of bismuth is unknown, take 15 grams of sample. Boil the resulting solution to eliminate oxides of nitrogen, cool it, and neutralize it with dilute ammonium hydroxide (1 + 1) until it is just alkaline to methyl orange indicator. Add sufficient nitric acid to give an acid concentration of about 0.02 *N*. Heat the solution to boiling, add 5 ml. of 20% potassium bromide solution and 3 ml. of 3% potassium permanganate solution, and keep boiling until the violet color of the solution vanishes. Filter out the precipitate of manganese dioxide on a Gooch crucible and wash it twice with 5-ml. portions of water. Add the same volumes of solutions of potassium bromide and potassium permanganate to the filtrate as before to obtain a second precipitate of manganese dioxide. Combine the precipitates and dissolve them in about 5 ml. of a mixture containing equal parts of dilute sulfuric acid (1 + 4) and 20% sodium sulfite solution. Add 4 ml. of 50% citric acid solution. Add dilute ammonium hydroxide (1 + 9) drop by drop until the odor of ammonia is barely perceptible. Add also 4 ml. of 50% solution of potassium cyanide.

Transfer the resulting solution to a separatory funnel, and add an excess of a solution of dithizone in carbon tetrachloride (5 mg. per 100 ml.) in 5-ml. portions from a buret, the dithizone having been purified by the ordinary method (*3*). Shake the separatory funnel vigorously after each addition of dithizone, and draw off the carbon tetrachloride phase each time before proceeding with the next addition of dithizone. Stop adding the dithizone solution when the green color of the solution remain unchanged for 1 minute. Collect the red dithizonates in another separatory funnel, and wash them with about 5 ml. of water. Add about 5 ml. of nitric acid (1 + 19). After vigorous shaking, draw off the carbon tetrachloride phase to a third separatory funnel and repeat the shaking with dilute nitric acid. Combine the acid extracts, add 2 drops of 0.04% *m*-cresol purple indicator, and neutralize with dilute ammonium hydroxide (1 + 9) until the solution is almost colored orange. Extract with fresh carbon tetrachloride in 5-ml. portions to remove the yellow oxidation products of dithizone, they being least soluble in water at about pH 3. Add about 0.2 gram of hydroxylamine hydrochloride to minimize the oxidation of dithizone. Readjust the pH of the solution by adding dilute ammonium hydroxide or nitric acid until the solution is colored orange (pH 3). Add the solution of dithizone in small volumes. Shake vigorously for at least 2 minutes. Draw off the orange bismuth dithizonate before the next addition. The end point is reached when the green dithizone solution remains unchanged in color.

Calibrate the dithizone solution against the standard bismuth solution every day. Prepare the standard bismuth solution by dissolving 0.1 gram of pure bismuth in nitric acid and then diluting to 1 liter. Take care to have sufficient nitric acid present so that no basic salt of bismuth is precipitated during the dilution. One milliliter of this solution contains 100 micrograms of bismuth.

ANALYTICAL RESULTS

To test this procedure, various amounts of bismuth were added to 25 ml. of acid copper sulfate solution (copper, 40 grams per liter; sulfuric acid, 184 grams per liter). The results (Table I) are one set of single determinations selected at random from several sets. In each determination a blank of 2 micrograms has been subtracted from the amount of bismuth found.

Analyses were also made with different forms of copper (Table II). These different forms do not come from the same source,

Table I. Determination of Bismuth in Acid Copper Solution

(1 ml. of dithizone solution equivalent to 13γ of bismuth)

Bi Added	Volume of Dithizone Solution	Bi Found	Error
γ	*Ml.*	γ	γ
10	0.65	9	−1
20	1.35	18	−2
30	2.35	31	+1
40	2.95	38	−2
60	4.35	57	−3
80	5.95	77	−3
100	7.35	96	−4

Table II. Determination of Bismuth in Refined Copper

Form	Bismuth Content, %
Copper sheet	0.0002
Copper shots	0.0007
Copper wire	0.00008
Copper powder	0.0018

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so that results are not comparable. The weight of sample taken varied from 5 to 25 grams. A blank of 2 micrograms was subtracted from the amount of bismuth found. The results have not been checked with other methods, but the author feels certain that the error is less than ±3 micrograms and that the relative error is less than 15%.

ACKNOWLEDGMENT

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Factors Affecting Determination of Potash in Fertilizers

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Evidence indicates that the presence of phosphate caused appreciably low results in the determination of potash by the official Lindo-Gladding method. Somewhat higher potash values were obtained when the phosphate was removed by precipitating with magnesium chloride. When freshly prepared sodium hydroxide solutions were used, the potassium chloroplatinate was contaminated with little or no water-insoluble residue. However, upon standing for some time, sufficient sodium silicate was produced by action of the alkali on the glass container to cause the formation of considerable residue.

IT WAS early observed that the presence of phosphate caused low results in the determination of potash by the Lindo-Gladding method. Methods proposed for the removal of phosphate include precipitating with magnesium chloride (*6*), magnesium oxide (*2*), and calcium carbonate (*3*). Bible (*1*) found that addition of sodium hydroxide before ignition prevented the etching of silica and porcelain dishes and permitted better recovery of potash from solutions of known potash content. Kraybill and Thornton (*6*) also concluded that the addition of sodium hydroxide effectively prevented the interference of phosphate. Recently, however, this conclusion has been questioned (*4*).

Another problem encountered in the Lindo-Gladding method is the occurrence of insoluble material in the potassium chloroplatinate precipitate. Kraybill and Thornton state that residue formation can be prevented by adding 0.6 ml. of hydrochloric acid to the alcohol with which the potassium chloroplatinate is treated after evaporation to dryness. It has been observed in this laboratory, however, that a residue usually remains after the potassium chloroplatinate is dissolved from the crucible with hot water.

The purpose of the work herein reported was to re-examine the problem of phosphate interference and to evaluate the error that may be encountered by failure to correct for impurities in the potassium chloroplatinate.

PROCEDURE

Experiment A. A solution of sodium phosphate was prepared such that 1 ml. contained the equivalent of 5 mg. of phosphorus pentoxide. Into platinum dishes were pipetted 25-ml. aliquots of a potassium chloride solution and sufficient sodium phosphate solution to introduce the equivalent of 0, 5, 25, and 50 mg. of phosphorus pentoxide per determination. Potash was determined by the official Lindo-Gladding method for potash in mixed fertilizers, except that the potassium chloroplatinate was dissolved out of the crucibles and determined by reweighing the crucibles. The potash contained in the phosphate solution alone was determined both by the Lindo-Gladding gravimetric method and by a modification of the colorimetric method of Sideris (*7*). These values appear in Table I as corrections to be applied to the total potassium chloroplatinate found in each determination.

Experiment B. Solutions of two 20% superphosphates (Laboratory Nos. LL5281 and LL5317) were prepared according to the official potash method. Then 25-ml. aliquots of a potassium chloride solution and of the superphosphate solutions were placed in platinum dishes and potash was determined as in Experiment A. Corrections for the potash in the superphosphates were determined both gravimetrically and colorimetrically.

Experiment C. In order to investigate the effect of removing the phosphate from solution, as advocated by some workers, the following materials were placed in four 250-ml. volumetric flasks:

Flask 1, 100 ml. of a potassium chloride solution.

Flask 2, 100 ml. of a potassium chloride solution and 2.5 grams of superphosphate (No. LL5317).

Flask 3, 100 ml. of a potassium chloride solution, 2.5 grams of superphosphate (No. LL5317), and 2.5 grams of magnesium chloride hexahydrate.

Flask 4, 2.5 grams of the superphosphate and 2.5 grams of magnesium chloride hexahydrate.

Flask 1 was made to volume with water.

Flasks 2, 3, and 4 were made up as potash solutions by adding ammonium oxalate, boiling for 30 minutes, adding ammonium hydroxide, and filtering. The insoluble materials from flasks 2 and 3 were dried and suspended in volumetric flasks which had been filled to the mark with water. The increase in volume due to the insoluble material from flask 2 was 0.7 ml. and the increase due to that from No. 3 was 1.5 ml. Thus the potassium ions

Table I. Effect of Phosphate on Potash Determination

Treatment	Total K_2PtCl_6 Found	Correction I Lindo-Gladding	Correction II Colorimetric	Corrected Value I	Corrected Value II	Loss I	Loss II
	Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
Experiment A, sodium phosphate							
KCl (ignited)	0.1409	....	....	0.1409	0.1409	....	....
KCl + 5 mg. P_2O_5	0.1408	0.0002	0.0005	0.1406	0.1403	0.0003	0.0006
KCl + 25 mg. P_2O_5	0.1410	0.0008	0.0025	0.1402	0.1385	0.0007	0.0024
KCl + 50 mg. P_2O_5	0.1411	0.0016	0.0050	0.1395	0.1361	0.0014	0.0048
Experiment B, superphosphate							
KCl (ignited)	0.0971	....	....	0.0971	0.0971	....	....
KCl + LL5281	0.1008	0.0053	0.0075	0.0955	0.0933	0.0016	0.0038
KCl + LL5317	0.0994	0.0036	0.0061	0.0958	0.0933	0.0013	0.0038
Experiment C							
KCl (ignited)	0.0967	....	....	0.0967	0.0967	....	....
KCl + LL5317	0.0983	0.0036	0.0061	0.0947	0.0922	0.0020	0.0045
KCl + LL5317 + $MgCl_2$	0.1030	0.0077	0.0094	0.0953	0.0936	0.0014	0.0031

Table II. Effect of Age of Alkali Solution on Residue Formation

Materials Analyzed	Alkali Used	Average Residue, Gram
No. LL5317	Freshly prepared	0.0001
	Two weeks old	−0.0001
	One year old	0.0023
	Two years old	0.0027
KCl (ignited)	One year old	0.0026
KCl + LL5317	One year old	0.0024
Eight mixed fertilizers	Freshly prepared	0.0005
	Two years old	0.0028

were dispersed in 249.3 and 248.5 ml. of solution, instead of 250 ml. The results have been calculated on the basis of these corrected volumes.

Potash values were obtained on the four solutions by the official method. In addition, the correction value (flask 4) was determined colorimetrically, as in Experiments A and B.

Experiment D. It was observed that when the amount of sodium hydroxide, which is added to the aliquot before evaporation, was reduced from 2 ml. to 1 ml. there was a decrease in the amount of residue left in the crucibles after dissolving out the potassium chloroplatinate. Since this indicated that the sodium hydroxide was responsible for at least part of the residue formation, the amount of residue formed was determined when alkali solutions of varying ages were used (Table II).

DISCUSSION

The data in Table I show that if the gravimetric correction for the potash in the phosphate source is used, the loss of potash is small, as has been reported by previous investigators, but, if the colorimetric correction is employed, the loss is appreciable. Experiments B and C (Table I) indicate an average loss of 0.0016 gram of potassium chloroplatinate when the gravimetric correction is used, and 0.0038 gram if the colorimetric correction is employed. Loss of these amounts of potassium chloroplatinate during determination of potash in a fertilizer by the official method would be equivalent to losses of 0.12 and 0.30% K_2O, respectively.

It is well known that 80% ethanol causes some loss of potassium chloroplatinate in the official method. For this reason alone the gravimetric correction is undoubtedly low. Furthermore, if there is a loss due to the presence of phosphate at the time of ignition, all the potash in the phosphate source will not be represented in the gravimetric correction value. It is the opinion of the authors, therefore, that the colorimetric method more accurately measures the amount of potash in the phosphate source, and that the loss of potash by the official method is greater than has been previously reported.

The data obtained in Experiment C indicate that removal of the phosphate by precipitating with magnesium chloride yields slightly higher potash values. Failure to obtain still higher values may be due to slight occlusion of potassium ions on the magnesium ammonium phosphate precipitate during the extraction process, as has been previously postulated (*1*).

The results summarized in Table II show that the sodium hydroxide solution is responsible for most of the residue formation that occurs. On treatment of the residue with hydrofluoric acid, 91.4% was volatilized, indicating that it was largely silica. Apparently the alkali solution on long standing reacts with the glass container. The sodium silicate thus formed becomes insoluble upon ignition and is not removed in subsequent operations.

In view of this effect of sodium hydroxide on residue formation, it would seem desirable to modify the official method: (1) to specify the use of a silicate-free (freshly prepared) sodium hydroxide solution, or (2) to recommend that the potassium chloroplatinate be dissolved out and the crucibles reweighed if the alkali is not prepared at frequent intervals.

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Apparatus for Preparing Samples for Analysis

Rapid Pulverizing and Mixing of Small Solid Samples

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A sample pulverizer is described which is designed for the rapid preparation of large numbers of 3- to 20-gram solid samples for analysis, with negligible contamination or loss of material. It is essentially a small high-speed hammer mill. A practical apparatus for mixing the pulverized samples, consisting of a weighing-bottle clamp rotated by a motor-driven shaft, is also described.

THE analysis of a large number of materials requires preliminary reduction of a 3- to 20-gram sample from an initial size of 4- to 8-mesh to 50-mesh or finer with negligible contamination or loss of material. None of the commercially available sample pulverizers is entirely satisfactory for this purpose. Those employing a motor-driven mortar and pestle are designed primarily to produce small amounts of finely divided material and do not lend themselves to the rapid pulverizing of large numbers of samples. Ball mills and mills of the disk-grinding type are not designed to operate with quantities of material as small as 3 grams and may cause undue contamination or loss of material if so used. The sample pulverizer herein described is a convenient instrument designed and built expressly to meet the above requirements. For use in conjunction with the sample pulverizer, a practical apparatus for mixing the pulverized samples is also described.

PULVERIZER

Description. The sample pulverizer, shown along with the sample mixer in Figure 1 and depicted diagrammatically in Figure 2, is essentially a small high-speed hammer mill with fixed (nonpivoted) hammers.

A one-piece four-armed rotor, *R*, whose arms function as hammers, is driven in the cylindrical pulverizing chamber at approximately 10,000 revolutions per minute by a direct coupled 0.125-hp. series type, 110-volt, 60-cycle, alternating current motor. The pulverizing chamber, 7.5 cm. (3 inches) in diameter and 1.9 cm. (0.75 inch) deep, is built into the steel block, *B*, and is equipped with a removable cover, *C*, held in place by spring clips, *P*, and retaining pins, and provided with a hopper and cock, *S*, for charging material into the chamber. The cock is turned through an angle of about 120 degrees to allow a small cavity in the cock alternately to fill with material from the hopper and to discharge this material through a channel into the chamber.

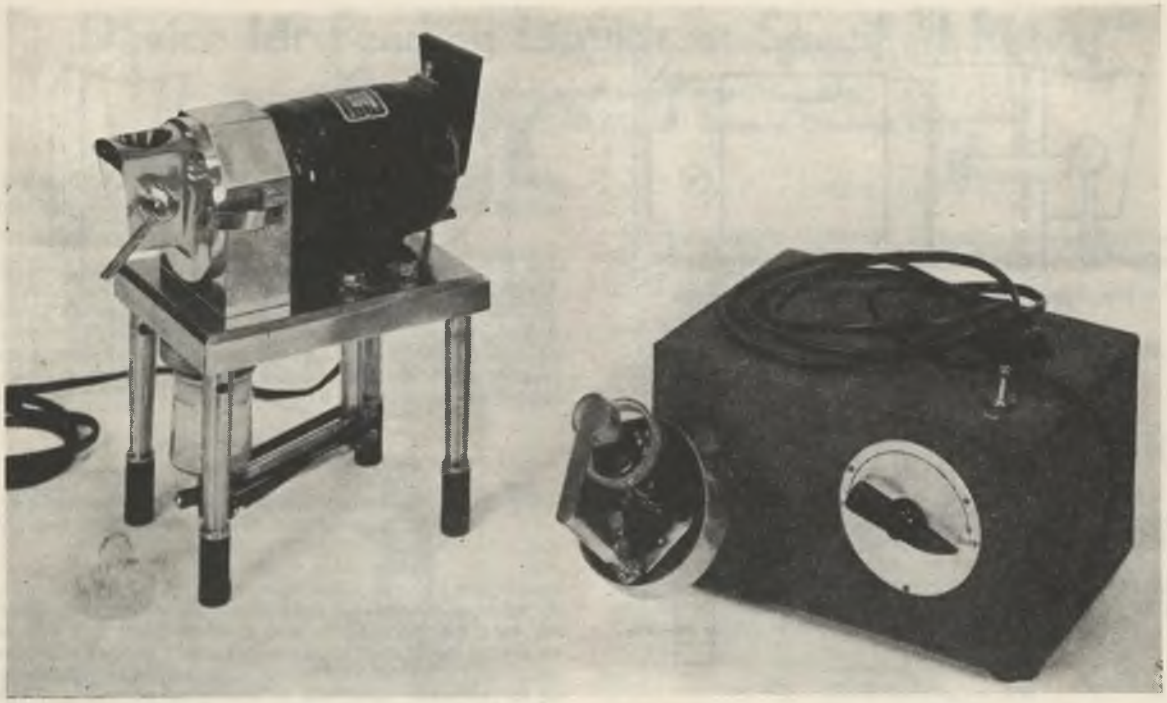

Figure 1. Sample Pulverizer and Mixer

This arrangement serves to prevent too rapid feeding of material and, at the same time, effectively to seal the channel, so as to prevent loss of dust during the pulverizing operation.

Upon entering the chamber, the material is picked up by the rotor and thrown against the cylindrical wall of the block. Pulverization is very rapidly achieved by successive impacts of the particles with the hammer and wall. The pulverized material passes through an interchangeable metal sieve plate, *E*, at the bottom of the chamber and falls through the sieve retainer and delivery tube, *D*, directly into a weighing bottle, *W*, which is held against the rubber cone, *F*, of the delivery tube by a spring clamp support. A rough control over the particle size of the ground product can be accomplished by use of sieve plates of varying degrees of fineness. However, hole diameters of 0.055 and 0.036 inch have been found generally suitable for soft and hard materials, respectively. Soft materials tend to clog the sieve plate when fine holes are used.

The pulverizing chamber is fitted with a replaceable sleeve liner which provides for a clearance of 0.02 mm. (0.008 inch) between the outer edge of the rotor arms and the liner. This liner, the rotor, and the inside surface of the chamber and cover are nitrided to produce a surface unusually resistant to wear. Furthermore, since the pulverizing action is due to impact rather than to grinding or shearing forces, contamination of the sample with iron is reduced to a minimum.

All parts of the hopper, cock, and sieve assembly can be quickly assembled or disassembled without the use of tools. All passages through which the material passes are readily accessible and can be cleaned by use of an ordinary test-tube brush followed by blowing with a stream of compressed air. The machine is easily inverted to facilitate cleaning; a small Bakelite guard plate attached to the rear motor housing prevents the toggle switch from coming in contact with the table top when the machine is inverted.

OPERATION. Completely assemble the cleaned apparatus. Turn on the motor and allow it to reach full speed. Place a clean weighing bottle tightly against the rubber cone of the sieve retainer and delivery tube and clamp the bottle in place by use of the spring clamp. Place the sample, crushed to 4-mesh or finer, in the hopper and feed portions of it into the pulverizing chamber by a 120 degree movement of the delivery cock, allowing the motor to regain full speed after each addition of material. When a sufficient amount of sample has been pulverized, stop the motor, disassemble the apparatus, and clean it by thorough brushing followed by blowing out with a jet of compressed air. Add the brushings to the main portion of the sample in the weighing bottle.

PERFORMANCE. The results of tests carried out to determine the efficiency of the sample pulverizer are summarized in Table I. It will be seen that the pulverizer is capable of reducing materials of hardness below that of quartz (H7) to powders substantially finer than 50-mesh and that the time required for the pulverization of 5 grams of material varies from 1 to 4 minutes, depending upon various properties of the material. The loss on milling is small and should have no effect on the composition of the sample. The percentage loss is reduced when larger samples are milled.

Quartz, although pulverized as rapidly as rock salt, is not reduced to as fine a state of subdivision and causes slight scratching and abrasion in the pulverizing chamber. Carborundum chips (H9.5) cause appreciable abrasion. This indicates that use of the pulverizer should be limited to materials of hardness below that of quartz (H7).

Iron is the impurity most likely introduced by the pulverizer. The contamination with iron is determined by the effective hardness of the pulverizing chamber and abrasive qualities of the

Table I. Operating Characteristics of Sample Pulverizer

Material	Hardness on Moh's Scale	Time to Mill 5 Grams	Loss in Milling	Screen Analysis of Product			
				20–50 mesh	50–100 mesh	100–200 mesh	Finer than 200 mesh[b]
		Min.	%	%	%	%	%
Rock salt	2.5	1.5	1.8	0.8	11.0	17.0	71.2
Activated alumina, 8–14 mesh	...	1	1.0	0.8	5.9	11.0	82.3
Activated alumina, 4–8 mesh	...	1	1.1	0.6	2.5	17.0	79.9
Activated alumina, 4–8 mesh[a]	...	3.5	2.1	0.0	0.4	12.0	87.6
Porocel	...	1	1.0	3.5	3.7	16.0	76.8
Marble chips	3	1.5	0.6	1.3	27.0	29.0	42.7
Marble chips[a]	3	1.5	3.8	0.0	3.7	21.0	75.3
Pyrex	6	1.5	1.2	3.6	21.0	32.0	43.4
Pyrex[a]	6	2.5	0.9	0.7	13.0	30.0	56.3
Iron pyrites	6–6.5	1	1.0	2.6	14.0	24.0	59.4
Quartz	7	1.5	0.9	5.0	16.0	29.0	50.0
Carborundum	9.5	4	Gain	6.5	14.0	31.0	48.5

[a] Sieve plate hole diameter = 0.036 inch; all other trials, hole diameter = 0.055 inch.
[b] By difference.

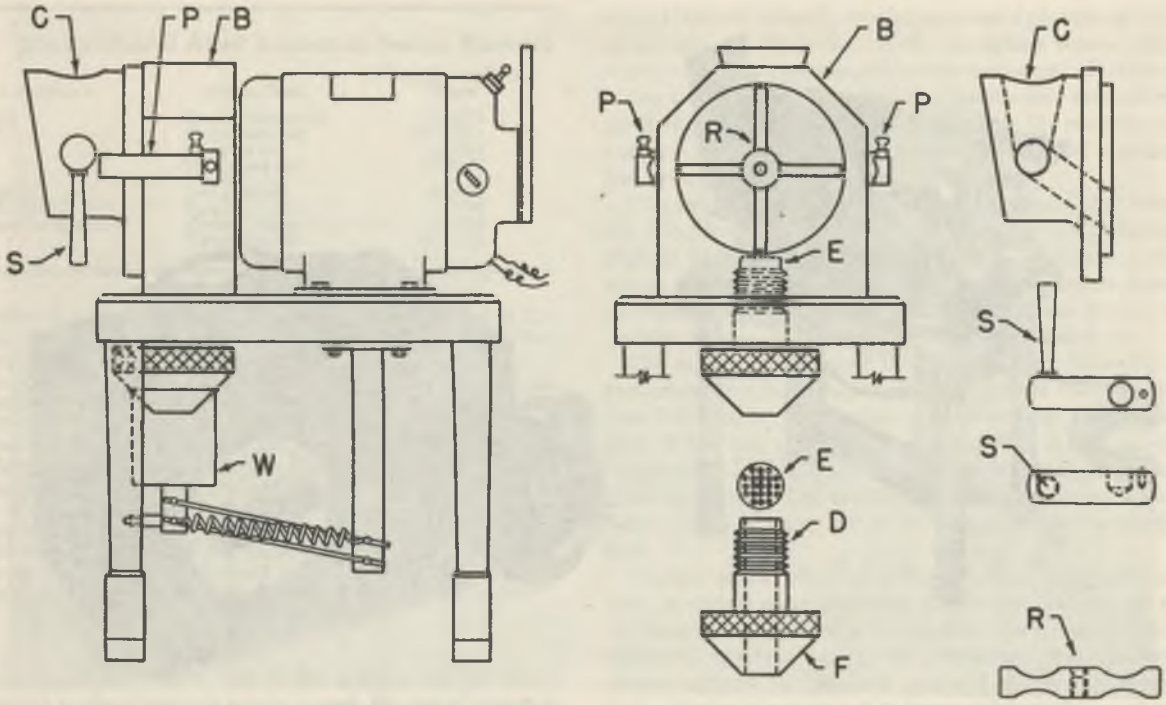

Figure 2. Component Parts of Sample Pulverizer

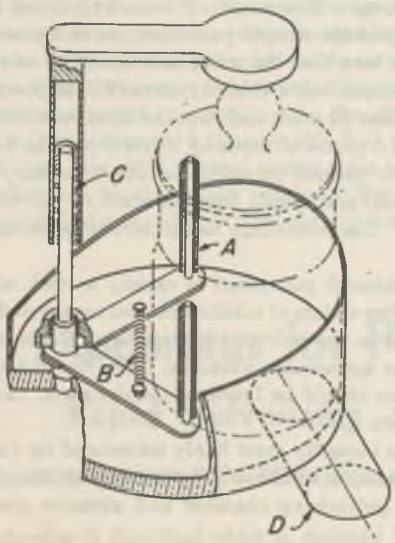

Figure 3. Construction Detail of Sample Mixer

Weighing bottle clamp

A.	Rubber tubing	*C.*	Compression spring
B.	Tension spring	*D.*	Horizontal shaft

sample. When the surfaces of the rotor and pulverizing chamber are uniformly nitrided, the contamination by iron is generally less than 0.01% for materials such as inorganic oxides, salts, and glasses (hardness less than 6).

Rock salt and Porocel tend to form adherent coatings on the inside of the pulverizing chamber. These coatings are difficult to remove by brushing but are easily removed by running a few grams of marble through the pulverizer.

SAMPLE MIXER

DESCRIPTION. The sample mixer, shown in Figure 1, consists essentially of a specially designed clamp mounted on a shaft which is driven through a 72 to 1 worm and pinion reduction gear by a 1/30-hp., 110-volt, universal type alternating-direct current motor. The speed of the motor is controlled by a series rheostat, so that the speed of the shaft can be varied at will between 30 and 150 revolutions per minute.

The clamp for holding the weighing bottle (Figure 3) is arranged so that the axis of the shaft passes slightly below the geometrical center of the weighing bottle and forms an angle of 135 degrees with the major axis of the weighing bottle. Thus, when the machine is turned on, any material in the weighing bottle is subjected to a motion such as to minimize segregation caused by differences in density, particle size, or particle shape.

The clamp is designed to hold the same weighing bottle receiver (which may be 20 to 40 mm. in diameter and 40 to 60 mm. high) used with the sample pulverizer. The glass-stoppered weighing bottle is held in place by a clamp and spring arrangement which automatically compensates for differences in diameter and height of the bottle and permits quick, easy placement or removal of the bottle. The clamp assembly is not damaged if the mixer is started when the weighing bottle is not in place.

The shaft is provided with an eccentric cam, and a small metal hammer connected to a tension spring is so placed that the hammer strikes the shaft a sharp tap twice during each revolution. This feature (not shown; inside the housing) is of value in loosening caked materials from the sides of the weighing bottle. The jarring effect can be regulated from zero to maximum by a thumbscrew adjustment.

PERFORMANCE. By use of the mixing device described above, highly satisfactory mixing of samples is obtained for the large majority of samples encountered. A number of tests have shown, however, that incomplete mixing may occur for certain types of samples, especially those which tend to form lumps. Satisfactory mixing can be achieved in these cases by stopping the machine once or twice during the mixing operation to break up the lumps with a glass rod.

Both the sample mixer and the sample pulverizer have been in use for more than three years preparing various types of inorganic material for analysis. During this period, performance has been entirely satisfactory and much time has been saved in the preparation of samples.

ACKNOWLEDGMENT

The authors wish to express their appreciation to T. N. Ravn and F. D. Tuemmler for their valuable suggestions during the development of this apparatus.

Device for Feeding Liquids at Specified Rates

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THE problem of feeding two liquids into a reaction vessel continuously in specified amounts may be solved by the apparatus shown in Figure 1.

Liquids of densities d_1 and d_2 which must be delivered in volumes v_1 and v_2 are contained in chambers 1 and 2, respectively. The pressure above the liquids, P_1, is sufficiently below atmospheric pressure, P, in the mixing chamber so that the liquids flow only when stopcocks 3 and 4 are opened and if air is bled into the apparatus through capillary tube 5 and bubbler 6. The relation between P_1 and P when stopcocks 3 and 4 are open and no liquids are flowing is

$$P_1 + d_1h_1 = P$$
$$P_1 + d_2h_2 = P$$

Since the pressure is the same above and below each liquid—that is, P_1 and P, respectively—it follows that

$$d_1h_1 = d_2h_2$$

Thus, the heights of the two liquids are inversely proportional to their densities. When air is admitted through the bubbler, P_1 decreases and this is offset by a flow of both liquids from the chambers. The rate at which the height of each liquid falls is inversely proportional to the densities of the liquids. Obviously the lighter liquid must be placed in the taller chamber, as its height will fall faster. The volume of liquid delivered depends on the cross-sectional area of the chamber; the radius of the chambers may be computed by the relations

$$\pi r_1^2 h_1' = V_1$$
$$\pi r_2^2 h_2' = V_2$$

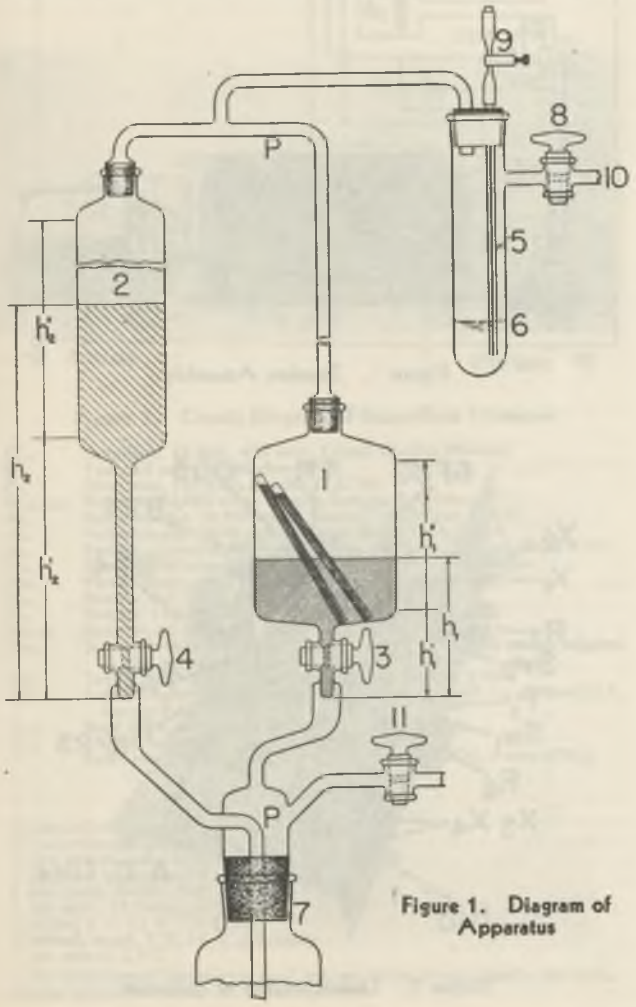

Figure 1. Diagram of Apparatus

and $$h_1'' = h_2'' \frac{d_2}{d_1}$$

In designing the apparatus, the dead spaces indicated by h_1' and h_2' cannot be used, but the apparatus should be constructed so that $h_1' = h_2' \frac{d_2}{d_1}$. A convenient size is chosen for r_1 and h_1'', and r_2 and h_2'' are then computed.

For illustration, consider the vapor-phase bromination of pyridine (*1*):

$$C_5H_5N + 2Br = C_5H_4NBr + HBr$$

The molecular weights of the pyridine and bromine are 79 and 2(80), the densities 1 and 3, and the volumes 79 and 53, respectively.

As it is necessary to have an excess of bromine the volumes selected are 80 ml. of pyridine and 65 ml. of bromine, which must be added slowly but in these proportions, the reaction taking place in the hot tube attached at 7. If it is desired to run a 6-mole batch, the volumes involved are 480 ml. of pyridine, V_2, and 390 ml. of bromine, V_1. A convenient radius for the pyridine chamber might be 2.4 cm.; and using

$$\pi r_2^2 h_2'' = V_2$$
$$(3.14)(2.5)^2 h_2'' = 480$$

it is found that $h_2'' = 23.7$ cm. h_1'' is then found from

$$h_1'' = h_2'' \frac{d_2}{d_1} = 23.7 \frac{1}{3} = 7.9 \text{ cm.}$$

and r_1 is calculated by

$$\pi r_1^2 h_1'' = V_1$$
$$(3.14)\ (r_1^2)7.9 = 390$$
$$r_1 = 4.0 \text{ cm.}$$

In practice the exact sizes of glass tubing for the chambers will not be available, but the chambers can be made approximately and the cross-sectional area of one or both adjusted by inserting glass rods. In the case of a dense material like bromine, glass rods will float, but a suitable rod can easily be made from glass tubing filled with wire solder or mercury and sealed.

The number of these rods required can be determined best by filling the chambers to heights h_1' and h_2' with water. Volume V_1 of water is then added to chamber 1 and V_2 to chamber 2. Height h_2'' is measured, h_1'' calculated by

$$h_1'' = h_2'' \frac{d_2}{d_1}$$

and the level of liquid 2 adjusted to the calculated height by adding glass rods.

To set the apparatus in operation volumes V_1 and V_2 are placed in their respective chambers, and the pressure above the liquids is decreased by applying suction at 10. With stopcock 8 closed and screw clamp 9 closed, stopcock 3 or 4 is cautiously opened and air allowed to bubble up through the liquid until it stops and liquid begins to drip out. Both stopcocks, 3 and 4, are then opened. An initial flow of one liquid will probably occur, automatically adjusting heights h_1 and h_2, so that

$$h_1d_1 = h_2d_2$$

after which the flow stops. Air is then admitted by opening screw clamp 9, which permits liquids in chambers 1 and 2 to flow. The bubbles of air passing are a convenient indicator for adjusting the rate of flow of the liquids.

The reaction vessel to which the apparatus is attached should be arranged so that pressure P remains constant. In the case of the bromination of pyridine, where the vapors pass over pumice in a tube, the accumulation of liquid on the pumice may cause the pressure to change slightly, disrupting the flow of the liquids from the chambers. In such a case a stopcock such as 11 placed on the mixing chamber can be left open to the atmosphere.

LITERATURE CITED

(1) Hertog and Wibaut, *Rec. trav. chim.*, 51, 381 (1932); U. S. Patent 1,977,662 (Oct. 23, 1934), assigned to Dow Chemical Co.

Alternating Current–Operated Thermionic Titrimeter with Adjustable Range and Sensitivity

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A stable, alternating current–operated, continuous reading, inexpensive vacuum tube voltmeter is described. It is simple in construction and operation. Its use as a titrimeter, a pH meter, and a direct current voltmeter is detailed. In the latter application it serves as a continuous reading potentiometer. It has a range of approximately 10 volts and a sensitivity of ±0.0001 volt. A calibration switch provides standard reference points for pH measurements. Independence of range and sensitivity controls make it versatile in electrochemical measurements with all the usual electrode systems, including the glass electrode.

THE analysis of complex mixtures of fireproofing agents for use on cotton cloth required the use of a sensitive electron tube titrimeter. An examination of the instruments commercially available and a review of those described in the literature showed that in general sensitivity and stability either had been sacrificed for the sake of simplicity or had been attained by the use of a complex and expensive circuit. With the objectives of continuous indication, line operation, stability, simplicity, low cost, and continuously adjustable but independent range and sensitivity control in mind, the instrument described below was developed. All parts were easily obtained except for the microammeter. However, a suitable meter is generally available at most colleges and research institutions. With a 60-microampere meter of low internal resistance the full-scale sensitivity may be varied from 59 to 10,000 millivolts, or, if employed as a pH meter, the scale either may be set to read over a pH range of, say, −1 to 15, or may be selectively set at any point over the range with full-scale sensitivity as great as one pH unit. That the titrimeter is line-operated is advantageous in that it eliminates the bother and delay of replacing batteries. Power consumption is only 30 watts. The cost of the materials used, exclusive of meter and electrodes, is approximately $30.

Goode (*14*) introduced the electron tube titrimeter in 1922. The subject of potentiometric titration up to 1930 has been reviewed in some detail by Furman (*9*). Naturally, the development of the titrimeter has followed progress in electronics (*1–5, 7–12, 14–18, 21–25, 27, 31–34, 36–38, 40*), but in general voltmeters having high enough input resistance, sensitivity, and stability to be used with glass electrodes are complex instruments with intricate controls. An exception to these complex circuits is that devised by Garman and Droz (*11*), which has only two controls. It is, however, battery-operated and has a sensitivity approximately one third of that attained by the present device, using a comparable meter. Furthermore, it is limited in range. The Garman and Droz apparatus is sold as the Leitz G and D Electrotitrator (*21*) with, however, the additional complication of a third interlocked control and other modifications.

The basic cathode follower circuit used here was proposed by Schmitt (*30*) in 1938, and should not be confused with the dummy tube balanced bridge circuit patented by Wold (*39*) in 1916. The present circuit eliminates the need for tubes of identical plate resistance and amplification factor (mu-balance) (*10, 35*). In addition to simplicity this circuit offers other advantages: (1) It effectively cancels the deviation from linearity of the curve relating anode current to grid voltage, which was found by McFarlane (*22*) to be as high as 1.5%. (2) The so-called "following" action of the cathode increases the input resistance of the instrument. Any potential applied to the control grid which would cause it to deviate from the free grid potential is reduced without decreasing sensitivity. This effect is discussed by Richter (*28*) and Rider (*29*). (3) It allows a method of range control covering a greater range than hitherto possible without complication of the electrical circuit and the method of adjustment. Further, this control has no effect on the sensitivity of the instrument. (4) It is stable to both gradual and quick changes of line voltage, as noted by Goldberg (*13*).

To obtain even greater stability than is afforded by the cathode follower circuit, the authors employ an alternating current stabilizing unit, introduced by Lampkin (*20*) to regulate the input of the power transformer. This is supplemented by conventional gas tube stabilization of the direct current supply voltages. Thus, not only the plate and bias voltages, but also the heater supply is regulated.

CIRCUIT AND ELECTRICAL CHARACTERISTICS

The apparatus is pictured in Figures 1 and 2. The electrical circuit, Figure 3, is drawn so that the titrimeter may be considered in three sections, *A*, *B*, and *C*.

Section *A* is the voltage-regulating circuit which stabilizes the voltage to the primary of the transformer that supplies power to the whole instrument. The proper operation of this section depends upon the adjustment of resistor R_9, which should be at the maximum resistance which allows both of the type 874 tubes to operate with their familiar violet glow at the lowest excursions of the line voltage. For a 115-volt line this will be about 100 ohms. At this setting they function properly over a range of input voltage of approximately 15 volts, say from 110 to 125 volts. The adjustment of R_9 can be made most conveniently while the instrument (with all tubes in their sockets) is plugged

Figure 1. Titration Assembly

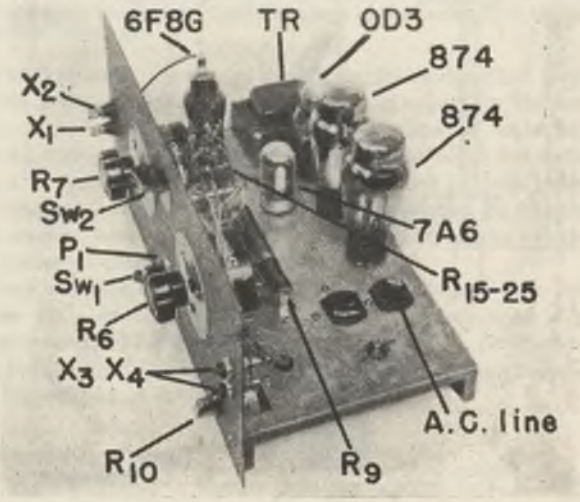

Figure 2. Chassis Layout of Titrimeter

into a variable-voltage transformer which is set for about 5 volts below normal line voltage. The action of the glow tubes reduces the voltage to the primary of the transformer to about 90 volts root mean square. Therefore, to provide the proper voltage for the 7A6 heater, the normal 6.3-volt winding of the transformer, which is now providing only 4.7 volts, must be augmented by an additional 1.8 volts from a 2.5-volt tap of another secondary winding, as shown in the circuit diagram. This is not done for the 6F8-G heater because 4.7 volts are sufficient for this application and the resulting low cathode temperature minimizes grid current due to thermionic emission and photoelectric effects. Of course, the voltage stabilizer may be used as a separate unit if provision is made to disconnect the transformer of the titrimeter.

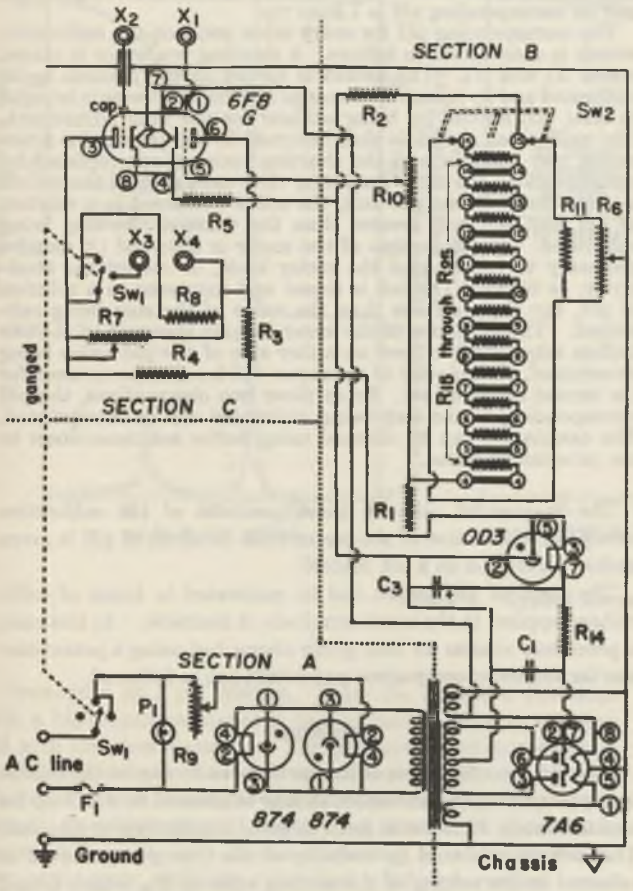

Figure 3. Circuit Diagram of Buras-Reid Titrimeter

$C_{1,2}$.	Capacitors, 16-mfd., 450 volts, Cornell Dunlier BR-1645
F_1.	Fuse, 0.5 ampere, Littlefuse 3AG
P_1.	Pilot lamp, 125 volts, 6 watts, G.E. S-6
$R_{1,2,3,4,5}$.	Resistors, 25,000 ohms, 5 watts, Sprague Koahlohm 5K
R_6.	Potentiometer, 10,000 ohms, General Radio Type 314-A
R_7.	Potentiometer, 5000 ohms, General Radio Type 314-A
R_8.	Resistor, approximately equal to meter resistance, 1/2 watt, IRC BW-1/2
R_9.	Resistor, 200 ohms, 25 watts, adjustable, Ohmite Dividohm
R_{10}.	Potentiometer, 10,000 ohms, 2 watts, Mallory A10MP
R_{11}.	Resistor, 600 ohms, 0.5 watt, IRC BW-1/2
R_{14}.	Resistor, 10,000 ohms, 1 watt, IRC BT-1
R_{16-25}.	Resistors, 25 ohms, 0.5 watt, IRC BW-1/2
Sw_1.	Switch, double-pole three-position, Federal 1424 (with springs adjusted to give proper action)
Sw_2.	Switch, 12-position, meter insertion type, Mallory 1400L
TR.	Power transformer, secondaries: 5-volt c.t., 6.3-volt c.t., 420-volt c.t., Stancor P-6289
$X_{1,2}$.	Input jacks, General Radio Type, 138-UL
$X_{3,4}$.	Output jacks, ICA 528
	Radio tubes, 2 type 874, 1 type 7A6, 1 type OD3, 1 type 6F8-G

ADDITIONAL PARTS

2 tube sockets, standard 4-prong base
2 tube sockets, octal base
1 tube socket, loktal base
1 dial lamp bracket and jewel
2 dial plates, 0–100, 300° rotation
1 dial plate, 12 index, 30° spacing
1 chassis, 6 × 13 × 1.5 inches
1 cabinet, metal, 7 × 14 × 7.5 inches
1 fuse mount, 3AG

The above-named brands were used, but any others of equal quality and similar physical dimensions would be satisfactory.

The load should be less than 15 watts and resistor R_9 must be suitably adjusted as just described. In a typical application, a 5-volt variation in line voltage causes a 0.06-volt change across a 5-watt capacitative load. On the other hand it may be desirable to use the stabilized power supply of sections A and B together to replace the battery supplies of other electrical devices.

Section B consists of the twin diode 7A6 operating as a full wave rectifier with its associated filter C_1, R_{14}, C_2, voltage-regulating tube OD3, and voltage divider for the various supply and control voltages. The condensers must have their terminals insulated from the chassis. Potentiometer R_{10}, the "zeroing control", provides the necessary operating potential for one grid of the 6F8-G tube and should be adjusted so that the indicating meter is at zero when the input terminals are "open circuited"—that is, when no connection is made to the input terminals. When this condition is attained, the input circuit is at the free grid potential when the meter indicates zero, no matter what voltage is applied to the input terminals. Potentiometer R_6, the range control, provides a continuously adjustable bucking potential which is used for balancing out the initial cell potential in potentiometric titration, and wherever only relative values of voltage changes are desired. The range covered by this control is approximately 1 volt, being governed by the shunting resistor, R_{11}. The range may be decreased or increased by using a lesser or greater resistance for R_{11}. The adjustment of the ratio R_6 to R_2 is critical, as is discussed below. The combination of the multiposition, or calibration, switch Sw_2 and resistors R_{16} through R_{25} composes a supplemental circuit for introduction of stepwise potential shifts into the input circuit by removal of series resistors from one side of R_6 to the other side without changing the total resistance of the divider. It is, in effect, a second independent range control, the steps of which can be standardized in terms of millivoltage or in terms of pH intervals and utilized in the calibration of the instrument, so that any desired pH range may be set on the meter without the necessity of referring to buffer solutions during each determination. This supplemental circuit may be omitted if the calibration feature is not desired.

Section C is a single-stage current amplifier of the cathode follower type. A microammeter is used to indicate unbalance of the triode sections with a potentiometer, R_7, to adjust sensitivity. This control is adjustable continuously from zero to maximum. A 2-pole 3-position switch, Sw_1, is used to provide off, stand-by, and meter positions. The stand-by or neutral position substitutes a resistor, R_8, for the meter. Thus, protection for the latter is provided when changing electrodes, etc., without upsetting thermal equilibrium.

An important factor in the measurement of potentials from high resistance cells, such as those containing a glass electrode, is the effective input resistance of the measuring instrument. In a typical application, 100.0 millivolts applied to the input grid through a resistance of 100 megohms (10^8 ohms) cause a deflection of the meter corresponding to approximately 99.8 millivolts. Similar behavior at other potentials allows the calculation of an approximate mean input resistance of 5×10^{10} ohms over the range of ± 0.4 volt of free grid potential. Hence, within this range, the instrument will respond with an accuracy of 1% of the full-scale sensitivity with cells of 500 megohms and with correspondingly greater or less error with cells of higher or lower resistance. It finds application, therefore, to all normal glass electrode circuits (*6*). If used at nearly maximum sensitivity, 60 millivolts equal to full-scale deflection, a 1-millivolt error would limit the application to cells of 800 megohms.

On the other hand, if the instrument is calibrated with the cell to be used, by means of standard buffer solutions, the error due to the shunting resistance of the input circuit is automatically corrected by an increase in sensitivity of the titrimeter, and the residual error, after correcting for electrode characteristics, is due to nonlinearity of the relationship of grid current versus grid potential.

With input circuits of low resistance, the over-all response, up to the meter, is linear within $\pm 0.05\%$.

The range control allows any voltage from -0.5 to $+0.5$ volt (pH -1 to 15) to be set at zero on the indicating meter and the sensitivity control allows full-scale sensitivity of from approximately 59 millivolts (1 pH unit) up to 10 volts, if a 60-microampere meter of low internal resistance is used. Any meter

from 0–1 milliammeter to a sensitive galvanometer can be used with corresponding sensitivity. Sensitivity also depends on the internal resistance of the associated meter.

Four meters have been used: (1) A 0–200 microampere Weston meter, Model 1, 544 ohms, gave a sensitivity of 1.1 microampere per millivolt, which corresponded to full-scale deflection (3.25 inches) of 180 millivolts (3 pH units), and was easily readable to 0.2 millivolt (0.003 pH unit). (2) A 0–60 microampere Simpson meter, Model 6718A, about 500 ohms, gave approximately the same sensitivity, which corresponded to a full-scale deflection (4 inches) of 59 millivolts (1 pH unit), and was easily readable to 0.1 millivolt (0.002 pH unit). (3) A 0–50 microampere Triplett meter, Model 626, 1900 ohms, gave a sensitivity of 0.7 microampere per millivolt, which corresponded to full-scale deflection (5.5 inches) of 72 millivolts (1.2 pH units), and was readable to 0.3 millivolt (0.005 pH unit). (4) A Leeds & Northrup mirror-type galvanometer with sensitivity of 0.0024 microampere per millimeter gave full-scale (1 meter) deflection, corresponding to 2.2 millivolts (0.04 pH unit).

Even at this extreme sensitivity there was greater variation due to building vibration, etc., than to amplifier instability. When operated within the limits of the built-in voltage stabilizer, it is practically free of error due to line-voltage variation; ±5 volts in the line corresponded to 0.6 millivolt (0.01 pH unit) in the input.

In use, the amplifier should be well away from the titrating apparatus, since mechanical shock to the chassis or tubes may introduce an error of the order of 3 millivolts (0.05 pH unit) due to semipermanent changes in the mechanical configuration of the 6F8-G tube. There should be no difficulty if 30-inch leads (one with grounded shield for the glass electrode, the shield being connected to the grounded jack plug) are used for both the input and meter connections and if the chassis is mounted on rubber feet. In this laboratory, the amplifier was placed on the stone reagent shelf just above the laboratory table and no trouble was experienced. In daily use, the average error observed corresponded to 0.25 millivolt input (0.004 pH unit) over a working day; so, if the instrument is to be used at its limit of sensitivity, it should be left on continuously and checked at calibration points at least once each day. It is under these conditions that its operation from line voltage is most appreciated.

Error due to surface leakage in the input circuit can be minimized by a direct lead to the grid cap, as has been used by some authors (*37*), or, if a more convenient type of connection is used as in the present instrument, by providing a well-insulated plug jack. The glass envelope of the 6F8-G tube should be coated with ceresin wax (*24*). The instrument is preferably constructed on a radio-type chassis mounted in a steel cabinet, as shown in Figures 1 and 2. In any case, complete shielding is necessary. The chassis and cabinet must be grounded, preferably through the "ground" of a three-wire system. (In other wiring systems with the ground wire fused, it may be advisable to use a shielded wire connected to the conduit to avoid voltage difficulties in case the fuse blows.) Failure to do this may cause irregular behavior of the meter due to body capacitance of the operator.

STANDARDIZATION OF CALIBRATION SWITCH

Although the most direct method of standardizing the calibration switch, Sw_2, consists in measurement of millivoltages, for pH work, it will be necessary to utilize buffer solutions of known pH with the particular glass electrode to be used. This is because there are small differences due to liquid junction potentials, deviation in the behavior of glass electrodes, etc.

In order to standardize the positions of switch Sw_2 and allow its 12 positions to serve as calibration points over the range approximately pH = 1 to 12, it is first necessary to determine the pH of a solution in which the particular glass electrode–calomel cell combination to be used produces zero e.m.f. After the titrimeter has warmed up the indication of the meter is brought to zero by means of the zeroing control with the input terminals unconnected, and the sensitivity at maximum. X_1 and X_2 are shorted with a connector and the meter is again adjusted to zero by the range control; the calibration switch is set at some intermediate position throughout this determination. The shorting connector is now replaced by connections to the cell (the shielded lead of the glass electrode goes to X_2) and it is immersed in a buffer solution of known pH, say, 3. The deflection of the meter is observed (it may be necessary to interchange the meter leads, or reduce the sensitivity, or both). The cell is rinsed and immersed in a second buffer solution of pH, say, 9. The deflection of the meter is again observed (in nearly every case the polarity of the meter must be reversed from that of the previous observation; if so, a negative polarity is assigned to the second reading). From these two observations, the pH corresponding to zero e.m.f. of the cell can be interpolated. The calculation should be checked using buffer solutions closer to the determined value, because for any given electrode there will be a departure from linearity over this range. The switch position of the nearest whole number to this pH is then chosen as the "rest position" of the calibration switch, and, of course, it corresponds to the pH just determined. For example, the determined pH may be 7.3; the seventh position of the calibration switch is then chosen for the rest position, and its corresponding pH is 7.3.

The corresponding pH for every other point on the calibration switch is determined as follows: A shorting connector is placed across X_1 and X_2. The switch is turned to the position to be calibrated and by means of the range control, the meter is brought to zero, full sensitivity being utilized for the final adjustment. The calibration switch is then returned to the previously determined rest position and the shorting connector is replaced by connections to the cell. Assuming that each step of the switch is approximately one pH unit, the cell is immersed in a solution of pH, say, 0.5 unit greater than the value of the step being calibrated. The deflection of the meter is observed (it may be necessary to interchange the meter leads, or reduce the sensitivity, or both). The cell is rinsed and immersed in a solution of pH, say, 0.5 unit less than the value of the step being calibrated. The deflection of the meter is again observed (if the two buffers selected have been on either side of the pH value being determined, the polarity of the meter will have to be reversed for the second observation). From these two observations, the pH corresponding to the step being calibrated can be interpolated. The calculation can be checked using buffer solutions closer to the determined value.

The manner of utilizing these positions of the calibration switch for calibration of the meter scale in terms of pH is given under "Operation as a pH Meter".

The steps of the switch can be calibrated in terms of millivoltage applied to the input terminals, if desirable. In this case, a procedure similar to that given above, but using a potentiometer for sources of comparison potentials, can be followed.

OPERATION

Prior to the utilization of the instrument in any of the following applications, the titrimeter should be allowed to warm up for approximately 30 minutes until thermal equilibrium is attained. This will be indicated by stability of the free grid potential as reflected in the setting of the zeroing control, R_{10}, which should be adjusted so that the indicating meter is at zero with the input open-circuited, as directed in the description of Section *B* under "Circuit and Electrical Characteristics" above.

Operation as a Titrimeter. In acid-base, precipitation, or oxidation-reduction titrations, the cell is connected to the electrode terminals and the meter pointer set at zero or other convenient point by means of the range control. The setting of the sensitivity control is dictated by experience. For the first run, maximum sensitivity is ordinarily used; in subsequent titrations, the sensitivity may be reduced according to the needs of the determination. After addition of the first few drops of titrating solution, the pointer may swing in the wrong direction. This is remedied by interchanging the meter leads. If the sensitivity is set too high and it is apparent that the meter pointer will travel off the scale, the titration is stopped for a moment and, with no change in sensitivity, the pointer is set back to zero by means of the range control. The titration may then proceed, making the appropriate scale addition each time. This technique is particularly useful when high sensitivity is desired over a considerable range, such as in the titration of polybasic acids, or when error due to grid current must be kept to a minimum. Another useful procedure is to set the meter at its highest reading, titrate to zero, interchange the meter leads, and continue, changing the sign of the reading.

Typical potentiometric curves and their corresponding increment graphs are shown in Figure 4. *A* represents a simple acid-

base titration using a glass-calomel cell and shows the relative change obtained with a simple dibasic acid, oxalic. *B* shows the precipitation curve obtained with a platinum-calomel cell by precipitating lead with potassium chromate. The results checked within 0.1% of those obtained gravimetrically. *C* was obtained by titrating acidified iodine with sodium thiosulfate using a platinum-tungsten cell. Slight changes in acidity or other conditions gave strikingly different curves but the large potential change always corresponded with the visual end point. The metal electrodes were cleaned before each titration with pure 3% hydrogen peroxide made alkaline with ammonium hydroxide.

means of the range control, final adjustment being made with sensitivity at maximum. The range control is left in this position, the sensitivity reduced to zero, and switch Sw_1 placed in the neutral position. The calibration switch is rotated to the position corresponding to the other pH to be used in calibration. Switch Sw_1 is moved to the meter position and the sensitivity is increased until the desired indication is obtained. (It may be necessary to interchange the meter leads.) With switch Sw_1 back in the neutral position, the calibration switch is returned to its rest position. All pH values within the range over which the meter has been set can now be read off of the meter when the

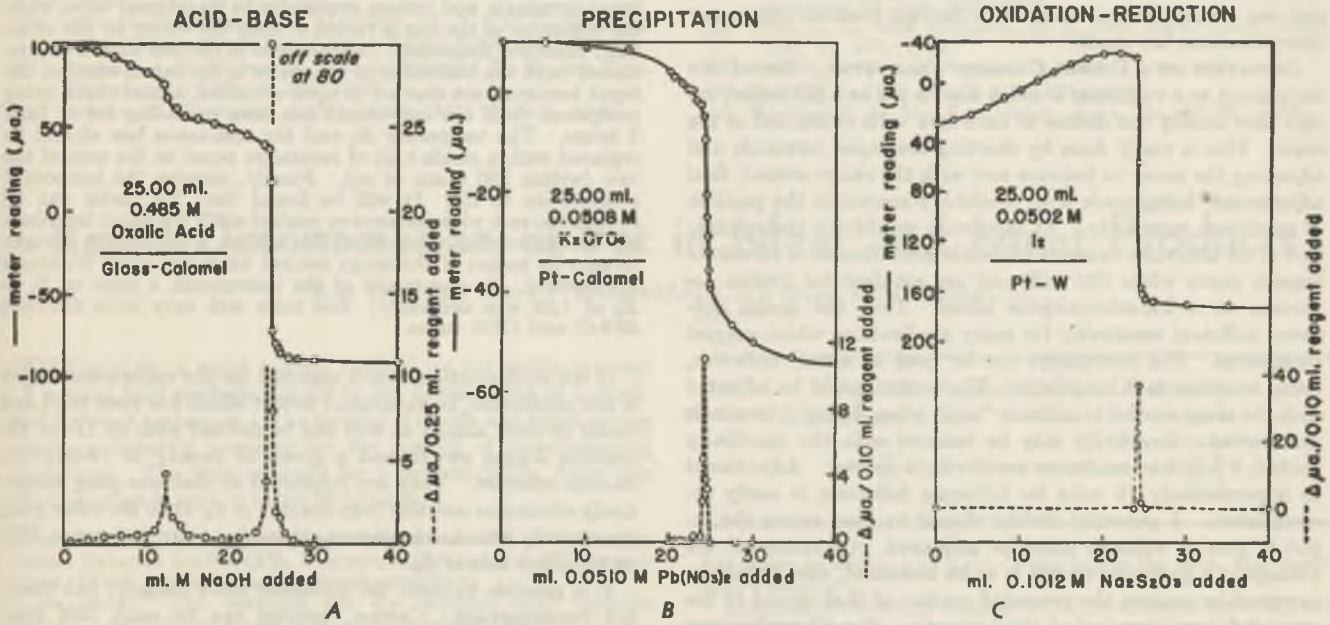

Figure 4. Typical Curves Obtained with Titrimeter

Operation as a pH Meter. Since the titrimeter functions with a high input resistance it can, of course, serve to measure pH with the glass electrode. The selective sensitivity makes it particularly suitable for small increments of pH, since a sensitivity of as little as one pH unit over the whole scale may be obtained. Out of four glass electrodes tried, there was a reproducible deviation from linearity in one amounting to ±0.5 pH unit on part of the scale, while the others had a full-scale random variation of only ±0.05 pH unit. It appears that any particular glass electrode should be checked and, if necessary, a correction curve plotted.

Setting the meter is simple. If buffer solutions are to be used, the procedure is as follows: It is desired to set the zero of the meter at pH 4.0 and to set another point on the scale at pH 7.0. The glass electrode and calomel half-cell, with the leads connected to X_2 (insulated) and X_1 (grounded), respectively, are placed in a buffer solution of pH 4.0. For this determination, the calibration switch remains in the rest position. The sensitivity control is advanced to full sensitivity, keeping the meter pointer at zero with the range control; the latter is left in this position. With the sensitivity control turned back to zero and switch Sw_1 in the neutral position, the electrodes are washed and placed in a buffer solution of pH 7.0. The switch is returned to "meter" position and the sensitivity control is turned up again until the pointer of the meter is at the desired point on the scale. (If the pointer swings in the wrong direction, the meter leads should be interchanged.) All pH values within the range of the meter are then determined by linear interpolation. It is advantageous to set the meter so that pH may be read without involved calculation.

If the calibration switch is to be used for setting the meter, the procedure is slightly different. The calibration switch is rotated to the position corresponding to the pH which is to be set at zero on the meter and a shorting connector is connected across the input terminals. The meter indication is brought to zero by shorting connector across the input terminals is replaced by the glass electrode–calomel cell.

However, it is not always desirable to set at zero one of the pH values available (either from buffer solutions or the calibration switch). This method of setting requires some calculation, but is not unduly complicated. For example, pH values of 4.2 and 7.2 are available and it is desired to set the pH of 4.2 at "42" on the scale and that of 7.2 at "72". The meter is set at 42 while the electrodes are in the solution of pH 4.2 (or while the input terminals are shorted and the calibration switch is in the appropriate position), the adjustment being made with both sensitivity and range controls, as necessary. Only experience can give the approximate settings and, once obtained, it is well to note these for future reference. With Sw_1 switched to neutral, the electrodes are rinsed and placed in the second solution (or the calibration switch is rotated to the other position). With Sw_1 back to meter position again a reading is taken. For example, the pH of 7.2 is at 92 on the scale. It is now necessary to reduce the "spread" or sensitivity from 50 scale divisions to 30 by means of the sensitivity control and return the pointer to its proper place on the scale by means of the range control. This may be calculated as follows:

$$S = \frac{B - A}{C - A} \times C$$

where S = new setting
A = lower scale value
B = desired higher scale value
C = observed higher scale value

or in the above example: $\frac{72 - 42}{92 - 42} \times 92 = 55.2$. This means that the pointer is moved from 92 to 55.2 by means of the sensitivity control. The range is now returned to its proper place by adjusting the range control so that the meter reads 72. The operation can be checked by referring back to the lower pH solution, or returning the calibration switch to its initial position.

A little experience is necessary to obtain approximately correct preliminary settings, since it is impossible to make calculations if the meter pointer goes off the scale with the second solution. It is desirable always to set the lower point on the scale first. Since range and sensitivity controls are independent, it is possible to shift from one pH range to another with no change in the full-scale interval—for example, if the instrument is adjusted to read from pH 0 to 7, then with the electrodes immersed in the solution of the latter pH, this value can be shifted back to zero by means of the range control and the meter then covers the range of pH 7 to 14. After calibrations involving the calibration control one should always return it to the rest position before any determinations are made.

Operation as a Direct Current Voltmeter. Use of the instrument as a voltmeter is much like its use as a pH meter, except that usually one desires to have zero volts at one end of the scale. This is easily done by shorting the input terminals and adjusting the meter to indicate zero with the range control, final adjustment being made with sensitivity control in the position of maximum sensitivity. At maximum sensitivity the application of 59 millivolts causes a full-scale deflection on a 60-microampere meter while 180 millivolts are required for similar deflection on a 200-microampere meter. Thus the device possesses sufficient sensitivity for many applications which suggest themselves. The instrument can be used as a null indicator, being sensitive to 0.1 millivolt. The meter should be adjusted with the range control to indicate "zero" when the input terminals are shorted. Sensitivity may be reduced with the sensitivity control, if less than maximum sensitivity is desired. Adjustment to approximately 10 volts for full-scale deflection is easily accomplished. A potential divider should be used across the input if greater voltages must be measured. Of course, if the voltage of a grounded circuit is to be measured, care should be exercised to connect the grounded portion of that circuit to the grounded input terminal of the titrimeter. For all applications in which true rather than relative voltages are required, the scale can be calibrated at "zero" and one other value (or at any two values when "zero" is off the scale) and all other values inserted by linear interpolation either by reference to external standard voltages or through utilization of the calibration switch previously standardized in millivoltages, if desired.

COMMENTS AND SUGGESTIONS

In the following section are given some facts which may prove helpful in the building and operation of the instrument.

There is some variation among type 874 gas tubes. If the instrument is plugged into a variable voltage transformer and the voltage changed, differences between tubes may be observed by noting the voltages at which they fire. The difference between firing voltages is subtracted directly from the effective range of the stabilizing unit, which is approximately 15 volts. During the development of the titrimeter, a 115-volt constant voltage transformer was used with satisfactory results. One could be substituted for the gas tube stabilizer (Figure 3, *A*) with, however, appropriate circuit changes to supply the proper filament voltages.

Instead of the 7A6 rectifier, a type 6ZY5-G tube can be used if resistor R_9 is adjusted to provide for the increased filament load and the proper tube socket is provided.

There is a difference in sensitivity between different 6F8-G tubes, a 10% variation being found in three tubes tested. There is also a tendency for this tube to respond to mechanical disturbances. If this should prove to be a serious handicap, two type 38 special nonmicrophonic tubes (which are connected as single triodes) could be substituted in the same circuit for the one double-section type 6F8-G tube which, unfortunately, is not made in a nonmicrophonic type (*26*).

In order that the range and zero controls may operate near their centers of adjustment, the required ratio of R_1 to R_3 should be determined as follows:

Permanently connect a 25,000-ohm (nominal) unit for resistor R_3. For R_1, lead two temporary connectors out of the instrument to a 25,000-ohm (nominal) resistor in series with a 9999-ohm decade resistance box. Also, temporarily ground both ends of R_{10} to the chassis. Short the input terminals, X_1 and X_2. Connect the meter as usual and observe a certain deflection of the meter which is practically independent of the resistance of the box in the circuit of R_1. (Interchange the meter leads or reduce sensitivity, or both, as necessary.) Note the sensitivity control setting, reduce it to zero, remove the shorting connector from the input terminals, and restore sensitivity to its original value while the resistance of the box is varied to keep the meter at the originally observed deflection. Adjustment of the box should be continued until the indication of the meter is the same, whether the input terminals are shorted or open-circuited, a final check being postponed until the instrument has been operating for at least 2 hours. The temporary R_1 and the resistance box should be replaced with a single unit of resistance equal to the sum of the two (within 250 ohms or so). Finally, remove the temporary connections to R_{10}. It will be found that the meter can be brought to zero with the zeroing control while the input terminals are unconnected and that when this is done, it can also be brought to zero by means of the range control when the input terminals are shorted. In one model of the instrument, a ratio of R_1 to R_2 of 1.08 was necessary; this ratio will vary with different 6F8-G and OD3 tubes.

If the multiposition switch specified for the calibration switch is not obtainable, an equivalent circuit which has been tried and found to work almost as well can be devised with an 11- or 12-position 2-gang switch and a group of twenty or twenty-two 25-ohm resistors. They are connected so that one gang successively eliminates resistors from one side of R_6 while the other gang successively introduces resistors of identical value (tolerance, 2%) on the other side of R_6.

It is possible to build the titrimeter more cheaply, but this is not recommended. Carbon resistors can be used, but wire-wound resistors are specified because they are inherently more stable. Inexpensive volume-control potentiometers were used in the first model for R_6 and R_7 and were fairly satisfactory. A cheap 2-pole, 3-position switch for Sw_1 should not be used, since leakage may develop. It would be better to eliminate the 3-position switch entirely by using a line-switch in conjunction with a meter switch. In this case the resistor, R_8, could not be used. The circuit has been designed so as to avoid the disadvantage of having a switch in the input leads.

The buffer solutions of Kolthoff (*19*) were generally employed as reference pH solutions because dilution has little effect on the pH and this is convenient in that the electrodes are usually wet.

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Rapid Determination of Fat in Meat and Meat Products

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THE need for a rapid control method for fat determinations in meat food products has led to the development of a modified Babcock technique. The method is simple and rapid, giving results sufficiently accurate for the control of manufacturing operations. The time required for a determination, when one Waring mixer is used, is about 30 minutes.

Apparatus. The apparatus required consists of a Waring mixer, Babcock bottles (8%, 18-gram, calibrated in 0.1%), cream pipet, 10-ml. graduate, and Babcock centrifuge.

Reagents. The reagents are c.p. sulfuric acid (specific gravity 1.84), glacial acetic acid, and household Oakite.

Procedure. Weigh out 25 grams of the finely ground sample, and place in a Waring mixer. Add 100 grams of cracked ice or water at 1° to 3° C., and 2 grams of household Oakite.

Run mixer 10 minutes with cover in place, stopping occasionally, to swirl contents and dislodge any lumps of meat which may adhere to the sides of the container. After thorough mixing, weigh 10 grams of the emulsion to the nearest 0.1 gram into a Babcock bottle.

Add 5 ml. of glacial acetic acid, and mix thoroughly in order to coagulate the protein. Then add 10 ml. of concentrated sulfuric acid, a little at a time, and swirl until all lumps are dissolved. At this point, add just enough hot water to form a layer above the acid mixture. The fat rises above the water layer, and charring is reduced to a minimum.

Next, add 5 ml. more of sulfuric acid, and mix. Centrifuge for 5 minutes at approximately 1000 r.p.m., then add hot water to the neck of the bottle, and centrifuge 2 minutes. Finally, add hot water to within 1 to 2 cm. of the top of the neck, and centrifuge 1 minute.

Immerse the bottle in water at 70° C., and read after 2 minutes, on a descending fat column. The column will begin to descend when the bottle is removed from the water bath. The column should be read from the top of the upper meniscus to the bottom of the lower meniscus, applying the calibrations on the bottle for this measurement. Multiply directly by 9.2, in order to convert to per cent of fat. A correction must be applied for the difference from exactly 10.0 grams in the weight of the sample used.

Table I. Comparison of Modified Babcock Method with Standard A.O.A.C. Soxhlet Extraction for Fat in Meat

Sample	A.O.A.C. Ether Extraction	Babcock Method
	%	%
Chopped pork	25.3	25.6
Chopped ham	27.3	28.4
Pork sausage links	41.5	41.4
Wieners	26.2	24.9
	27.0	26.9
Chopped ham	25.9	26.7
	25.6	26.1
Bulk pork sausage	48.5	48.2
Chopped ham	25.6	26.2
Bulk pork sausage	45.5	45.5
	49.1	47.5
Chopped ham	24.6	24.9
	27.7	27.1
	25.3	25.8
Wieners	22.1	22.4
	22.2	22.5
	26.0	26.3
	22.0	22.3
	22.1	21.8.
Pork sausage links	41.6	41.4

Table II. Reproducibility of Method

Determination No.	% Fat
1	26.8
2	26.3
3	26.2
4	26.9

Comparisons were made between the official A.O.A.C. fat extraction method (*1*) and this rapid method. Samples run included chopped ham, chopped pork, bulk pork sausage, and wieners (natural and artificial casings), the fat content of which ranged from 20 to 50%. Based on an average level of 30% fat, the new method showed a standard deviation of ±0.7% with a probable error of ±0.5%, when compared to the A.O.A.C. method.

The comparative figures are given in Table I.

The difference between the Babcock values given above, and the values obtained by multiplying the reading on the Babcock bottle by 9.2, is caused by the fact that where exactly 10.0 grams of sample were not used, the fat values were corrected to exactly 10.0 grams.

The reproducibility of the method is indicated in Table II. Four separate determinations were made on the same sample. The maximum variation between determinations in this range was 0.7%.

This method gives satisfactory results with all types of fresh or cooked meat items, with the exception of foods of high cereal content. The cereal is not digested and forms a layer below the fat layer which interferes with the determination. In such a case, satisfactory results have been obtained by immersing the bottle in boiling water. The fat layer usually rises above the cereal, and satisfactory readings are obtained.

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Low-Lag Toluene Thermoregulator

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THE conventional glass mercury-toluene thermoregulator suffers because of the poor heat conductivity of the glass, which gives rise to an appreciable thermal lag. For use in high-precision, isothermal bomb calorimetry, a constancy within ±0.001° C. is desirable, and for this purpose a specially designed regulator using a thin copper container for the toluene was constructed and found satisfactory. The most important feature of this regulator is the means of obtaining a successful glass-to-metal seal (Figure 1).

To one end of a 3.0-cm. length of 2-mm. Pyrex capillary tubing is sealed a 5.0-cm. length of glass tubing 10.0 mm. in diameter. This is the end in which the adjustable contact is eventually placed. To the other end of the capillary is sealed a 30.0-cm. length of 60-mm. diameter tubing. Just below the end of the capillary, about 3.0 cm. of the 6.0-mm. tube are given a heavy coat of platinum deposited from the usual platinic chloride–oil of lavender solution by heating with a blast lamp. The platinum is then given a very heavy dense electroplating of copper from a sulfate bath. This completed glass part is shown at *a*, Figure 1. *b* and *c* were turned from hard-drawn copper bar stock. The walls of these pieces are made as thin as possible to obtain some degree of flexibility. The bore of *b* is made to fit snugly on the copper-plated section of the glass tube. Then *b* and *c* are brazed together to form part *d*. The double cup resulting is slipped over the copper-plated part of the glass tube, *e*, and the tube is connected to a steam source. After the whole has reached steam temperature, Wood's metal is allowed to flow into the joint, using dilute hydrochloric acid as a flux. After cooling, a perfectly tight seal between copper and glass results.

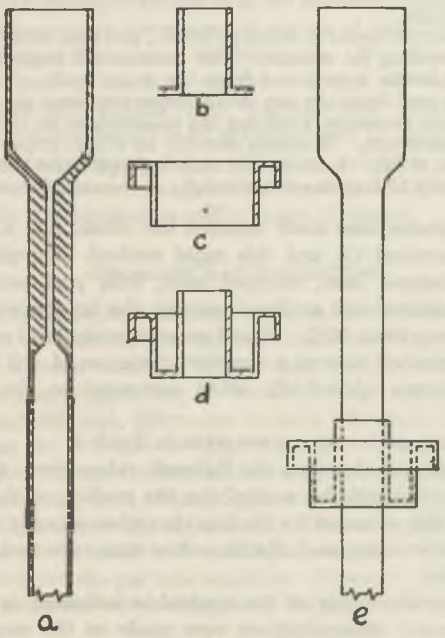

Figure 1. Details of Glass-to-Metal Seal

The next step consists in making the head and body of the regulator (Figure 2). *a* is turned from brass and is 5.0 cm. in diameter and 2.2 cm. thick. The hole is such a size (1.5 cm. in diameter) that the bottom of *d*, Figure 1, is a snug fit in it. The groove in the top is made so that the outer cup of *d*, Figure 1, fits in it loosely. For this, the groove is 22.0 mm. in diameter and 5.0 mm. deep. *b* is made of 2.5-cm. inside diameter hard-drawn copper tubing 26.0 cm. long with a bottom brazed on. *c* is a glass cup, about 5.0 cm. long and 2.5 cm. in diameter, fitting inside *b*, and cemented in with pyroxylin cement. The copper wire, *d*, is brazed to the inside of the copper tube and to the lower end of it is welded a length of platinum wire which reaches into the cup where, in the final assembly, it makes contact with the mercury.

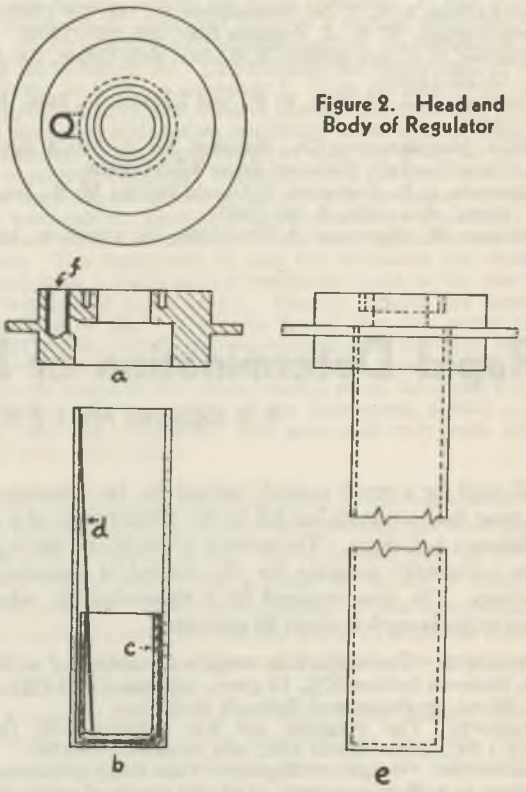

Figure 2. Head and Body of Regulator

The assembled body is now placed in the recess in the lower side of the head and soldered tight. This gives the nearly completed regulator shown in *e*.

The final step is to install the glass tube. The head is heated gently until Wood's metal can be melted in the groove, which is then filled almost to the top. Dilute hydrochloric acid is again used as a flux. The glass tube is inserted in the hole in the head as far as it will go. This causes the inverted part of the double cup to seat in the groove. Immediately the head is cooled with a damp cloth, so that the molten Wood's metal solidifies before that between the cup and the glass melts. The assembly is now complete.

In order to fill the regulator, a measured amount of mercury is placed in the glass cup by way of the glass tube. This amount is such that the lower mercury level will be about in the middle of the cup at operating temperature. Purified toluene is then run through the threaded hole at *f*. When full, a screw is tightened in the hole, using a lead washer to obtain a mechanical seal. Then the screw and washer are soldered to the head with Wood's metal.

This regulator in conjunction with a suitable electronic relay circuit will hold the temperature of a bath to within 0.001° C. for hours at a time. One contact of the regulator is grounded to the bath fluid. This drawback can be taken care of by using an isolation transformer in the relay circuit.

Geiger-Counter X-Ray Spectrometer

The first Geiger-counter focusing spectrometer to be developed has been announced by the North American Philips Co., Inc., 100 East 42nd St., New York, N. Y. It provides a new method of making quantitative and qualitative analyses of crystalline and certain amorphous substances in the paint, chemical, ceramic, rubber, and metallurgical fields; under optimum conditions of resolution accuracy of ±0.03° is obtainable.

Growth Stimulants for Microbiological Biotin Assay

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The microbiological determination of biotin (using *L. casei*) has been investigated from the standpoint of growth stimulants. The lipoid nature of such interfering factors in rice polish was established by comparing extracts that had been treated by filtration, ether-extraction, enzyme digestion, etc. Methods for obviating the stimulating effect have been devised. Various supplements to the basal medium were tested but none was found worthy of recommendation. Lecithin, mineral oil, oleic acid, whole rice oil, and the unsaponifiable fraction of rice oil were compared as to extent of stimulation produced. In tubes showing high acid and cell production in the presence of basal medium and rice oil without added pure biotin, no evidence of biotin synthesis could be demonstrated.

THE occurrence of a drift or anomaly in the assay of certain substances by microbiological procedures involving *L. casei* has been observed previously.

Growth stimulants and inhibitors have been noted for the Snell and Strong (*17*) riboflavin determination (*1*, *2*, *7*, *8*, *14*, *19*, *21*) as well as for two (*13*, *20*) pantothenic acid procedures (*5*, *9*, *10*, *11*, *12*). On the other hand, according to Strong and Carpenter (*19*), the nicotinic acid assay of Snell and Wright (*18*) employing *L. arabinosus* is scarcely affected by substances producing marked drift in the riboflavin and pantothenic acid assays, although there is some controversy as to the specificity of the Snell and Wright method (*3*). Interfering materials reported in the above references appeared to be largely lipoid in nature; however, bran suspensions and water-soluble constituents have been indicated as growth stimulants. Recommendations for the obviation of the drift effect in the riboflavin and pantothenic acid assays have provided for the removal of the lipoid material by solvent extraction or filtration and in some cases specified the use of an enzyme digestion. Oleic acid, one of the fatty materials indicated as a stimulant, has been shown to influence the growth of the diphtheria bacillus also (*6*).

In the use of the Shull, Hutchings, and Peterson (*15*, *16*) microbiological biotin assay with rice products, the authors have observed marked anomaly in the results obtained for rice of various degrees of milling as well as for brown rice, rice bran, and rice polish, the latter exhibiting the effect to the greatest extent (*22*). At the time it was felt that the interfering factors were present in the water-soluble fraction rather than the fat-soluble since analysis of defatted rice polish continued to show a drift effect. Evidence obtained later proved this conclusion to be erroneous and attributable to incomplete extraction of the rice polish. The study of this effect as produced by rice polish was then conducted to determine the nature of the stimulating constituents, methods of avoiding their influence, and the effect of several lipoid materials, some of which have proved to be stimulatory for *L. casei* in the riboflavin and pantothenic acid assays.

EXPERIMENTAL

The biotin assays were carried out as proposed and later revised by Shull, Hutchings, and Peterson (*15*, *16*). The same lot of rice polish, carefully sifted and mixed, was used throughout the experiments. Weighed samples of rice polish were suspended in normal sulfuric acid and autoclaved for 30 minutes under 6.8 kg. (15 pounds) of pressure. Samples of rice polish hydrolyzed by this procedure gave assay values in excellent agreement with duplicates hydrolyzed in 4 *N* hydrochloric acid for 2 hours at 6.8 kg. (15 pounds) of pressure. Hydrolysis for 30 minutes with normal acid, hence, was preferred because of its time-saving advantages. Repeated extraction of the same sample of rice polish and analysis of the combined extracts gave biotin values no higher than those secured through a single extraction. The biotin content of this particular sample of rice polish was well above average (*22*).

LOCATION AND REMOVAL OF INTERFERING SUBSTANCES. The following extracts were prepared, in order that the interfering or stimulating substances might be located and their removal effected.

Preparation 1, Rice Polish Suspension. A 1-gram sample of rice polish was autoclaved as described above in 50 ml. of normal sulfuric acid and cooled. The pH was adjusted to 6.8, the mixture made up to a volume of 1 liter, and diluted 1 to 4.

Preparation 2, Rice Polish Extract, Filtered. A suspension was prepared as in No. 1, filtered after being made up to a volume of 1 liter, and diluted 1 to 4.

Preparation 3, Defatted Rice Polish Suspension. Rice polish was extracted with petroleum ether in a Soxhlet extractor for 6 hours; 0.9 gram of the extracted polish was then suspended in normal sulfuric acid, autoclaved, neutralized, and diluted as in No. 1. Nine-tenths gram of defatted polish corresponded to 1 gram of ordinary polish in weight of nonlipoid material.

Preparation 4, Defatted Rice Polish, Filtered. Before the final dilution was made for No. 3, a quantity of the suspension was filtered and then diluted one to four.

Preparation 5, Rice Polish Suspension, Ether-Extracted. Before the final dilution was made in Preparation 1, a quantity of the suspension was extracted twice with 100-ml. portions of ethyl ether and then diluted 1 to 4.

Preparation 6, Defatted Rice Polish Suspension, Original Fat Content Restored. Nine-tenths gram of defatted rice polish was extracted, neutralized, and diluted to 1 liter. A 25-ml. aliquot was transferred to a 100-ml. volumetric flask and 1 ml. of a solution of 0.5 gram of rice oil in 200 ml. of 0.95% ethyl alcohol solution was added. The volume was made up to 100 ml. with distilled water.

Preparation 7, Rice Polish Suspension, Enzyme-Digested. After acid hydrolysis of the sample, the pH was adjusted to 4.5 with 2.5 *M* sodium acetate and the following substances were added: 1 ml. of taka-diastase suspension (20 mg. per ml. in cold water) and 1 ml. of papain suspension (equal weights of papain and glycerol mixed to a paste and dispersed in water—20 mg. papain per ml. of solution). Benzene (0.5 ml.) was added, and the solution was stoppered and incubated for 48 hours at 37° C., then neutralized and made up to appropriate volume (*4*).

The data obtained from the use of these preparations appear in Table I and Figure 1, expressed as apparent biotin content in relation to concentration of extract in assay tubes.

PREPARATION OF SUPPLEMENTED BASAL MEDIA. The basal medium was prepared as described by Shull, Hutchings, and Peterson (*15*, *16*) and to it were added the following supplements in an attempt to secure a standard growth curve that would correspond to the growth obtained with the unmodified rice polish extracts and by which the latter could be assayed without preliminary filtration, etc.

Supplement 1: 0.25 gram of biotin-free, defatted rice polish per liter of basal medium. Polish concentration in the basal diet then equaled that in a rice polish suspension at the dilution used for assay.

Table I. Apparent Biotin Content of Rice Polish Samples Corresponding to Different Concentrations of Extract

Rice Polish Extract	Prep. 1	Prep. 2	Prep. 3	Prep. 4	Prep. 5	Prep. 6	Prep. 7
Ml./tube	*Micrograms of biotin per gram of rice polish*						
0.25	2.77	1.00	0.98	0.90	1.84	2.88	1.92
0.50	2.20	0.98	1.04	0.96	1.28	2.32	1.84
0.75	1.88	0.98	0.88	0.96	0.96	1.87	1.55
1.00	1.65	1.07	0.91	1.00	0.92	1.64	1.48
2.00	1.22	0.90	0.89	0.96	0.82	1.10	1.40

Table II. Apparent Biotin Content of Rice Polish Sample as Calculated from Supplemented Basal Media Standard Curves

Rice Polish Extract	Normal Basal (Fig. 2)	Supplement 1	Supplement 2	Supplement 3	Normal Basal (Fig. 3)	Supplement 4	Supplement 5
Ml./tube	*Micrograms of biotin per gram of rice polish*						
0.25	..	..	.....	..	2.72	0.40	1.92
0.50	2.24	1.88	Off curve	1.92	1.92	1.04	1.44
0.75	1.87	1.71	Off curve	1.65	1.84	1.42	1.42
1.00	1.73	1.64	Off curve	1.60	1.65	1.32	1.29
2.00	1.32	1.35	0.86	1.25	1.58	1.40	1.32

Table III. Effect of Various Lipoid Substances on the Apparent Biotin Content

Substance	Weight per Tube	Weight of Added Biotin per Tube	Apparent Biotin Content per Tube
	Micrograms	*Micromicrograms*	*Micromicrograms*
Lecithin	20	0	110
	20	200	330
	160	0	560
	160	200	910
Mineral oil[a] (Marcol)	10	0	35
	10	200	190
	80	0	40
	80	200	310
Oleic acid	20	0	250
	20	200	440
	160	0	1000[b]
	160	200	1000[b]
Whole rice oil	20	0	230
	20	200	395
	160	0	1000[b]
	160	200	1000[b]
Unsaponifiable rice oil	20[c]	200	460
	40[c]	200	600

[a] Mineral oil was used at half the concentration of other materials because of its limited solubility in alcohol.
[b] These values represent approximations since the acid production exceeded maximum normal amount. The only value that could be assigned for the recovery calculation was that of the upper limit of the standard curve.
[c] Calculated from data on the percentage of unsaponifiable material in rice oil.

Supplement 2: 0.025 gram of rice oil in 0.95% ethyl alcohol per liter of basal medium. Oil concentration equaled that in a rice polish suspension of the concentration used for assay.

Supplement 3: 100 ml. of biotin-free aqueous rice polish extract, prepared like the yeast filtrate originally specified for the basal medium (*15*), per liter of basal medium. Water-soluble substances from the rice polish were present in sixfold concentration as compared with rice polish extract of comparable dilution.

The growth curves resulting from the use of these basal media with increments of pure biotin are shown in Figure 2. The apparent biotin content of a rice polish suspension (corresponding to Preparation 1) as read at several concentrations from these curves is given in Table II.

Subsequent to obtaining the data appearing in Figure 2 and Table III two additional supplements were prepared.

Supplement 4: 0.0025 gram of rice oil in 0.95% ethyl alcohol per liter of basal medium. Oil concentration was one tenth that in rice polish suspension at the dilution used for assay.

Supplement 5: 0.016 gram of mineral oil (Marcol) in 0.95% ethyl alcohol per liter of basal medium.

The growth curves for Nos. 4 and 5 are shown in Figure 3 and the corresponding apparent biotin content of a rice polish suspension (corresponding to Preparation 1) calculated at several concentrations from the curves is given in Table II.

Recovery Experiments. The following substances were prepared as colloidal suspensions in 0.95% ethyl alcohol and added to tubes containing either 0 or 200 micromicrograms of biotin: lecithin, mineral oil (Marcol), oleic acid, whole rice oil, and the unsaponifiable fraction of rice oil. The data obtained from these determinations appear in Table III.

DISCUSSION

Location and Removal of Interfering Substances. From the data appearing in Table I and plotted in Figure 1, several observations may be made.

Preparations 1, 2, 3, and 6 show that the interfering substances were located entirely in the fat-soluble fraction of the rice polish. Filtration of rice polish suspension or ether-extraction of rice polish prior to aqueous extraction was equally effective in elimination of the stimulating effect, as may be seen from the data for Preparations 2 and 3. Digestion of the autoclaved rice polish suspension with taka-diastase and papain gave assay values in better agreement with each other at various dilutions than did the rice polish control, but all values so obtained were too high, as shown by the filtered and ether-extracted samples (comparison of Preparations 7, 2, and 3). Neal and Strong (*12*) observed an increase in the pantothenic acid assay of certain samples after enzyme digestion and attributed the occurrence to the liberation of interfering substances, possibly fat-soluble in nature. The high biotin values obtained above in the enzyme-digested samples might have resulted from a similar release of stimulants.

Ether-extraction of the aqueous rice polish suspension (Preparation 5) left appreciable quantities of stimulating substances still in the extract. This particular operation was made somewhat difficult by the precipitation of considerable quantities of gelatinous material and the formation of an emulsion when ether was added to the water extract. Considerable stimulation is shown in the tubes containing small quantities of Preparation 5. Filtration of the suspension of defatted rice polish and analysis of the filtrate showed that all interfering substances had been removed in the initial ether-extraction of the dry polish (Preparations 3 and 4). Preparation 6 shows that the restoration of the defatted rice polish to its original fat content by the addition of rice oil in 0.95% ethyl alcohol produced a curve almost identical with that of the rice polish control, thus demonstrating further that the rice oil contained the interfering materials.

For the case of rice polish, then, simple filtration of the aqueous extract satisfactorily removed the interfering materials and was not improved upon by ether-extraction of either the dry polish or the extract itself. These findings are in general agreement with those of other workers (*2*, *12*, *19*).

Effect of Supplementing Basal Medium. Figure 2 demonstrates that no appreciable improvement in the basal medium was

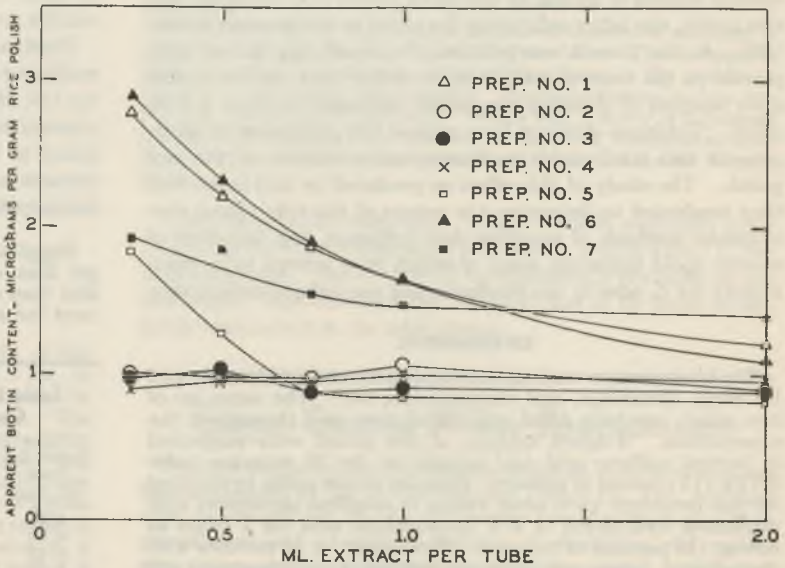

Figure 1. Apparent Biotin Content of Rice Polish Samples Corresponding to Different Concentrations of Extract

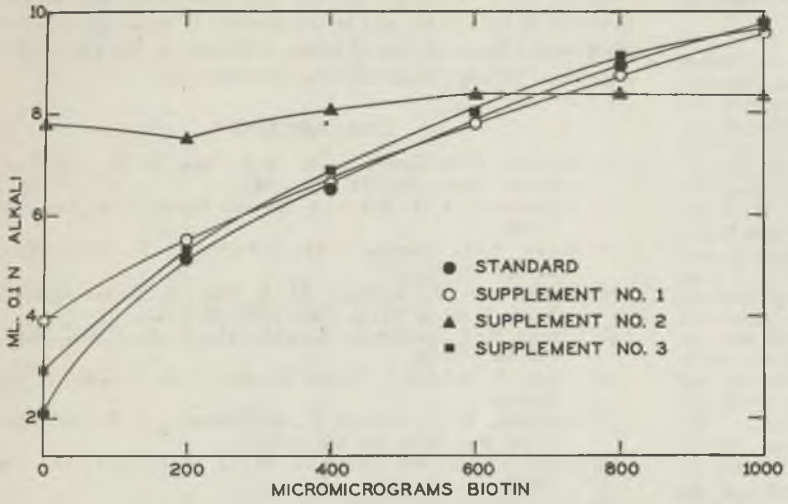

Figure 2. Response of *L. casei* to Supplemented Basal Media in the Presence of Biotin

secured by the addition of biotin-free rice polish or defatted, biotin-free rice polish suspension. The slight increase obtained by the addition of the aqueous extract probably corresponds to small quantities of biotin that were not destroyed by the peroxide treatment, just as slight deviations from standard shown by the suspension-supplemented curve can be attributed to incomplete removal of fatty substances. Values for rice polish suspensions (Table II) calculated from the three curves agreed reasonably with each other for each separate dilution considered, but the drift effect was still apparent, regardless of the curve used as standard. The assay values as determined at the 2-ml. level were unsatisfactorily high, as could be seen by comparison with a corresponding sample, Preparation 1, and the other preparations in Table I.

The addition of rice oil in 0.95% ethyl alcohol at the concentration given in Supplement 2 produced a rather remarkable growth curve. Near-maximum acid production was obtained throughout the length of the curve irrespective of the amounts of pure biotin present, even in the absence of added biotin. To the authors' knowledge this is the first report of such a phenomenon. The production of high amounts of acid in the presence of no added pure biotin was displayed by *L. casei* under the influence of lipoid substances other than rice oil (Table III) and is discussed below.

Since lesser amounts of rice oil than those included in Supplement 2 stimulated less than maximum acid production (Table III), two further supplements were prepared as previously described and the resulting growth curves appear in Figure 3. Both the rice oil–supplemented and the mineral oil–supplemented media gave curves reproducing the normal standard curve in general shape. The rice oil supplement showed stimulation at low concentrations of biotin, again even in the absence of pure biotin, but approached the normal curve at high concentrations. Unlike the curve obtained with Supplement 2 (Figure 2) the "standard" curve obtained with Supplement 4 revealed that acid production in the latter case was influenced by the amount of biotin present as well as the amount of rice oil. The mineral oil produced a somewhat constant amount of stimulation over the entire length of the curve (Supplement 5) except in the absence of pure biotin. Its behavior was similar to that reported for lecithin by Bauernfeind and co-workers (*2*) in their study of growth stimulants in the microbiological assay for riboflavin and pantothenic acid. The use of these supplemented media in the assay of a sample of rice polish yielded erratic results, as shown in Table II. On the whole none of the supplements used improved the basal medium or aided in removing the drift effect in assays of sample prepared by hydrolysis alone. Wegner, Kemmerer, and Fraps (*21*) reported similar findings in their work with the microbiological riboflavin assay.

Recovery Experiments. The five substances tested (lecithin, mineral oil, oleic acid, whole rice oil, and unsaponifiable fraction of rice oil) all produced stimulation to greater or lesser extent in tubes containing no added pure biotin as well as those containing 200 micromicrograms of biotin (Table III). The stimulation shown in tubes containing added mineral oil was of questionable significance with the exception of the tube containing 200 micromicrograms of biotin and 80 micrograms of mineral oil. That mineral oil does influence the growth of *L. casei* was illustrated in Figure 3. However, the amount of stimulation in relation to the weight of mineral oil added was small in comparison with the stimulation obtained with a comparable quantity of rice oil (Figure 2).

The addition of 160 micrograms of oleic acid or whole rice oil to tubes containing either no added biotin or 200 micromicrograms produced acid exceeding the highest level of the standard curve, but the apparent biotin content had to be reported as 1000 micromicrograms per tube, this value being the maximum given by the standard curve. Whole rice oil and oleic acid were approximately equal in stimulating effect, and lecithin was slightly less than either. The stimulating substances in rice oil were demonstrated to be present in the unsaponifiable fraction as well as the whole oil. Contrary to the results reported by Bauernfeind *et al.* (*2*) for oleic acid and lecithin, both of these substances were shown to stimulate acid production in the presence of no added pure biotin. Actually, of course, the basal medium cannot be considered to be entirely biotin-free since the yeast filtrate contains unremoved traces of the vitamin. The acid measured in the inoculated and incubated zero tubes of the standard curve exceeds the titratable acidity of a comparable quantity of basal medium, although the inoculum is prepared so as to be biotin-free. It is

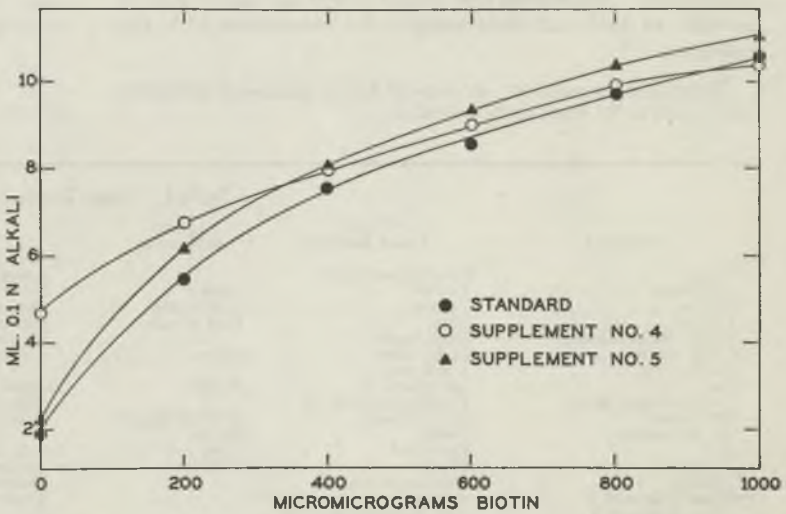

Figure 3. Response of *L. casei* to Supplemented Basal Media in the Presence of Biotin

shown, thus, that some biotin is present in the basal medium although none is added to the tube.

To discover whether or not synthesis of biotin had taken place in tubes containing no added pure biotin but showing maximum acid production under stimulation of lipoid substances the following flasks were prepared: (1) basal medium alone, (2) basal medium plus rice oil in quantity comparable to that present in rice polish extract, and (3) basal medium plus crystalline biotin comparable to that in standard tubes containing 800 micromicrograms of biotin. After inoculation and 72 hours' incubation, the flasks containing the rice oil and the pure biotin greatly exceeded the blank control flask in both acidity and turbidity. The contents of all three flasks were made 4 *N* with concentrated sulfuric acid and autoclaved at 15 pounds' pressure for 2 hours. Vigorous hydrolysis was carried out to ensure the liberation of cell contents. After hydrolysis the pH was increased to 6.0 by the addition of hot barium hydroxide octahydrate suspension. The precipitate was digested, filtered, and washed. The filtrate and washings were concentrated by evaporation, then made up to one fifth of the original volume. This concentrate was assayed at the 2-ml. and 5-ml. levels. In the case of all three concentrates, the 5-ml. level proved to be too high in dissolved materials to permit satisfactory growth of the organisms. The 2-ml. levels, however, showed the following sharp differentiation in milliliters of 0.1 *N* sodium hydroxide required for titration: (1) basal medium alone, 1.80 ml. of alkali; (2) basal medium + rice oil, 1.39 ml. of alkali; and (3) basal medium + pure biotin, 9.10 ml. of alkali. The results were checked by duplicate determinations.

It was concluded that no synthesis of biotin had taken place in the various tubes and flasks showing maximum acid production in the presence of rice oil and no added pure biotin. It is possible that the bacteria had somehow adapted themselves to an environment either biotin-free or containing ordinarily insufficient quantities of biotin. Work is being continued on this phase of the problem.

SUMMARY

Growth stimulants in the microbiological biotin assay have been investigated and methods for their removal devised.

Various supplements for the basal medium were studied, but none has been found worthy of recommendation.

Assay tubes showing high cell and acid production in the presence of stimulants and in the absence of added pure biotin were tested for evidences of biotin synthesis on the part of the organism. No synthesis could be demonstrated.

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Color Test for Oils and Resins, Using Hirschsohn Reagent for Cholesterol

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THE Hirschsohn reagent for cholesterol is useful as a simple color test for oil types. It also gives color reactions with some resins. When using this reagent in making tests, it is good practice to have authentic samples for comparison with the unknown.

Hirschsohn reagent for cholesterol (*1*), 9 grams of trichloroacetic acid and 1 cc. of distilled water.

PROCEDURE. Place 1 or 2 drops of an oil or a corresponding amount of resinous material on a porcelain spot plate, add 3 or 4 drops of the reagent, and wait a short time for the color to develop. As the color develops rather slowly at 20° C. or less, the test may be speeded up by warming the spot plate to 35° C.

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Table I. Color Test for Oils

Material	Color, 1 to 2 Minutes	Color, 5 Minutes
Oils		
Tung	Gels, gel turns red	...
Synthenol	Yellow	Brown
Isoline	Yellow	Slight pink
Linseed	Blue	Blue purple
Heavy-bodied linseed	Dark brown	...
Corn (maize)	Light blue	Purple
Neat's-foot	Light pink	...
Soy	Dirty blue	Purple
Cold pressed castor	Practically no color	...
Cottonseed	Light purple	Medium purple
Blown castor	Orange	Brown
Fish	Dirty red	Blue
Perilla	Mauve	Violet
Oiticica	Gels, gel turns red	...
Tung 3, linseed 1	Gels, gel turns brown red	...
Tung 1, linseed 3	Gels, gel turns light red	...
Tung 1, linseed 9	Red	Brown red
Resins		
Rosin	Blue green	Dark blue
Ester gum	Red	Purple
Cyclohexanone formaldehyde	Bright red	...
Cumar	Light red	...
Staybellite (hydrogenated rosin)	Light blue green	...
Varnish		
Ester gum, tung oil	Dark red	...
Ester gum, perilla	Brown	Purple
Dried varnish film		
Linseed type	Brown	Brown red
Dehydrated castor type	Light yellow	...
Tung type	Practically no color	...