ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

Your Division Is a Live Organization

THE great International Chemical Conclave, to be held in New York City in September 1951, is still more than a year away, but those responsible for formulating and developing the scientific sessions already are reporting definite plans for the A.C.S. Jubilee Meeting and the International Congress of Pure and Applied Chemistry.

H. H. Willard, chairman-elect of the Division of Analytical Chemistry, has announced that the following symposia will be held during the week of the 75th Anniversary Meeting of the AMERICAN CHEMICAL SOCIETY:

Chemical Kinetics and Mechanisms
Chairman: Frederick R. Duke
Chemistry Department
Iowa State College, Ames, Iowa

Physical and Chemical Equilibria
Chairman: Ernest H. Swift
Chemistry Department
California Institute of Technology
Pasadena 4, Calif.

Absorption and Emission of Radiant Energy
Chairman: Wallace R. Brode
National Bureau of Standards
Washington 25, D. C.

Microchemistry
Chairman: E. W. D. Huffman
505 Majestic Building
Denver 2, Colo.

Economic Aspects of Chemical Analysis and Manufacturing
Chairman: Beverly L. Clarke
Merck & Co., Inc.
Rahway, N. J.

Nucleonics and Tracer Techniques in Analytical Chemistry
Chairman: C. J. Rodden
U. S. Atomic Energy Commission
New Brunswick Laboratory
New Brunswick, N. J.

Polarographic Methods
Chairman: James J. Lingane
Chemical Laboratory
Harvard University
Cambridge 38, Mass.

The selection of subjects for symposia was made only after several *ad hoc* sessions of the executive committee of the division were held. We believe analysts will agree that the topics are timely and important. Dr. Willard is to be congratulated for his splendid selection of chairmen. He reports excellent cooperation and widespread enthusiasm from all those he has consulted in planning the symposia.

All the division programs at the 75th Anniversary Meeting of the Society will consist of symposia. General meeting papers will be given before the Congress. Beverly L. Clarke of Merck & Co., Inc., Rahway, N. J., has accepted the chairmanship of the Section on Analytical Chemistry.

And now to turn for a moment to the Chicago meeting this fall. The highlights of the program of the Division of Analytical Chemistry are: (1) two symposia on "Methods for the Determination of Water" and "Analytical Methods Based on Heterogeneous Equilibria," the latter in conjunction with the Division of Physical and Inorganic Chemistry, and (2) two round-table discussions: "Determination of Oxygen in Organic Compounds by the Unterzaucher Method" and "Analytical Distillations."

V. A. Aluise will act as moderator at the round table discussion on the determination of oxygen in organic compounds, and the panel will consist of H. S. Conway, W. H. Jones, W. H. Smith, C. C. Harris, and H. K. Alber. Arthur Rose will conduct the discussion on analytical distillations, and assisting him will be W. J. Podbielniak, F. D. Rossini, R. F. Marschner, R. M. Kennedy, and F. E. Williams.

The experiment of round-table discussions was such a pronounced success when tried at Atlantic City a year ago that the program committee felt it was highly desirable to arrange a similar program for Chicago. The same plan of reporting the round table discussions adopted for the Atlantic City meeting will be followed in Chicago. Stenotypists will be present. From these extensive reports the moderators will prepare two- or three-page summaries of the highlights for publication in ANALYTICAL CHEMISTRY.

The vitality of the Division of Analytical Chemistry is reflected in the programs just reviewed. Congratulations are in order to the officers of the division, and to those busy individuals who have accepted the duties of chairmen of symposia. A great amount of time and effort must be expended to develop such outstanding scientific programs. The principal reward is the satisfaction of knowing the division is thriving, and the enthusiasm of analysts never has been at a higher pitch than it is at this time.

THE ANALYTICAL PROCESS IN CHEMISTRY

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The basic stages in the analytical process are discussed with emphasis on the acute problems of isolating the material in a state suitable for measurement of the desired component and of making the measurement itself. The former problem is considered on the basis of the general techniques available for separating and segregating substances by chemical and physical methods. The process of measurement as applied to chemical substances is considered on the basis of the discriminatory power of the type of measurement used—i.e., ability of the measurement to distinguish between different substances. Fundamental principles of physical measurement as used in analysis are outlined.

THERE have been many previous attempts to classify the subdivisions and operations involved in the process which we call chemical analysis. One of the most thoroughly explored of such analyses of chemical analysis is that of Mellon (*2–5*), who discusses previous attempts at classification. Building on the foundation laid by Mellon, the analytical process has been analyzed in order to define the fundamental operations involved and learn how these operations are interconnected.

It might be asked why any attempt should be made to discuss the fundamentals of analytical chemistry from the viewpoint of its organization. The reasons for emphasizing fundamentals are the same as those for any method of classification: It summarizes available knowledge and leads to the discovery of new knowledge. Thus, it is hoped that a systematic investigation of he bases of analytical chemistry would indicate new analytical possibilities such as promising avenues for research, the development of better control methods, and the application of new techniques to the solution of analytical problems. In addition, a consideration of the bases of analytical chemistry should lead to a better understanding of the value and meaning of analytical data and therefore to a better use of analytical chemistry. Analytical chemistry, as we well recognize, is not an end in itself but a means to an end, and a better comprehension of the means will inevitably lead to more valuable results, thus yielding more fruitful analytical data.

Before proceeding, it would be in order to define what we mean by analytical chemistry. Analytical chemistry, as previously defined by the author, may be considered as comprising all techniques and methods for obtaining information regarding the composition, identity, purity, and constitution of samples of matter in terms of the kind, quantity, and groupings of atoms and molecules, as well as the determination of those physical properties and behavior which can be correlated with these objectives.

In essence, then, analysis is the application of analytical chemistry to obtaining qualitative and quantitative information about the nature of matter at the individual limit of the atomic level or higher.

THE ANALYTICAL PROCESS

The analytical process in chemistry can be considered as consisting of four principal stages of operation.

1. Sampling
2. Isolation (separation) of the desired constituent in a measurable state
3. Measurement of the desired constituent
4. Calculation and interpretation of the numerical data

It is obvious that under certain circumstances operations 2 and 3 may be combined. As Mellon has pointed out, the first three operations are essentially combined when the service station attendant performs the all-too-familar analytical process of determining the percentage of antifreeze in one's auto radiator by withdrawing a sample into a hydrometer. Usually, the interpretation of the result is known beforehand; another quart of antifreeze is necessary.

The most difficult portion of the analytical process is that involving isolation of the desired constituent in a measurable state. The actual process of measurement is usually simple. For example, in the determination of carbon in various types of materials, the process of isolation of the carbon as carbon dioxide is the difficult step; measurement of the carbon dioxide once formed is relatively simple and may be identical for different types of materials and separation processes. Thus, carbon in steel is converted to carbon dioxide by oxidation at high temperatures, while the carbon in organic compounds is converted to carbon dioxide after a relatively low-temperature combustion process; limestone is treated at still lower temperatures with acid to liberate carbon dioxide, while carbon dioxide may be removed from blood by the Van Slyke technique at room temperature.

In this connection the following pertinent sentences occurred in an article (*1*) on the semiannual report of the U. S. Atomic Energy Commission:

> Much of the chemist's work in the field of atomic energy comes under the deceptively simple heading "chemical separation." The separation or extraction of one material from another, or more often from a mixture of others, had to be resolved in order to make the bomb possible. Similarly, future progress is dependent on more effective means of carrying out complex separations. In this work, the chemists have studied all known methods for separations, including selective solvent extraction, distillation, precipitation, ion exchange, and liquid-liquid extraction.

We now consider the four component steps of the analytical process with particular attention to the role of current and future development in making analytical chemistry more useful.

SAMPLING

The first operation of sampling, paradoxically enough, has been much better developed for plant practice than for research operations. The fundamental requirement of any analytical sample is that it be representative of the mass of material whose composition is to be judged in terms of the behavior of the particular sample. The magnitude of the problem can be summarized in the standard method for the determination of the calorific value of coal, in which a carload of some 50 tons of coal may be reduced to a 1-gram sample which is burned in the calorimeter. This represents a reduction in size of 45,000,000 grams to 1 gram. The precision or reproducibility of the sampling process is evidenced by the fact that the permissible difference set by the American Society for Testing Materials is 0.3% for the same laboratory and 0.5% for different laboratories.

Methods of sampling for materials used in production and for many types of common products, as well as for certain types of

products concerned in the human economy, have been carefully standardized. Organizations such as the American Society for Testing Materials, the Association of Official Agricultural Chemists, and the American Public Health Association have done much to develop valid sampling techniques. In research and in much chemical production, though, we are still inclined to use "grab" sampling, assuming the material to be homogeneous within the desired accuracy of the experimental results. We tend to overlook the possible heterogeneity that may exist in small scale samples—for example, that due to relative particle size distribution where the particles may not all be of the same type. The organic chemist crystallizes or "salts out" 200 grams of his product; he then takes his spatula, picks up a few crystals at random on the tip of the spatula, and transfers this sample to a vial which is submitted for analysis. He assumes that his mass of crystals is homogeneous; he overlooks the possibility that salts have crystallized out with his organic product or that undesired organic materials have crystallized out during the early or late stages of crystallization of the main product. There is a serious need to educate the average research chemist as well as chemical engineer to the need of obtaining valid—i.e., representative—samples; the analytical data will be no better than the care exercised in sampling.

ISOLATION IN A MEASURABLE STATE

After a suitable sample has been secured, subsequent operations are usually concerned with the preparation of the sample for measurement. In essence, this process represents for the analytical chemist an attempt to separate the measurable properties of the desired constituent from those of the other constituents present. Such operation can be based only on the distinguishing properties, chemical or physical, of the substances concerned. Consideration of the processes that are used in separating the desired constituent so that it can be measured leads to several schemes for such classification. Thus, Mellon has classified the methods of separation as consisting of the following four types: volatilization, precipitation, electrochemical, and extraction. To the present author it has seemed that what the chemist actually does, in practice, is to isolate the desired constituent either by chemical treatment or by a mechanical separation of phases which may be preceded by phase formation or competition. Accordingly, the following classification of processes of isolation is suggested.

Separation through Chemical Environment. A common way of permitting the measurement of a component in the presence of interfering materials is to alter the chemical environment in which the measurement is to be made. The use of complex formation in removing cations from the possibility of action or reaction is well known—e.g., immobilization of ferric iron in the iodometric determination of copper by the addition of fluoride ion to form a ferric fluoride complex. In the polarographic analysis of organic compounds, variation in pH can be used to permit selective measurement; thus, maleic and fumaric acids can be determined in the presence of each other in alkaline but not in acidic solution.

Mechanical Separation of Phases. This type of separation is a simple and fundamental one in chemical operations and includes such familar operations as filtration, dialysis, diffusion (both thermal and gravitational), sedimentation, electrophoresis, magnetic and hand "picking," and the mass spectrometer. It is well to emphasize that the primary function of the mass spectrometer is to separate a group of heterogeneous phases on the basis of their mass-to-charge ratios; when the group of ionized particles passes through the magnetic field of the mass spectrometer, the result is a segregation into separate groups, each consisting of phases with the same mass-to-charge ratio. The principle of the mechanical separation of phases can be summarized in the following equation, where x denotes the desired constituent present in phase P_2, in a process by which a mixture of phases is separated into less heterogeneous groups by a suitable technique such as one of those mentioned:

$$P_1, P_2(x) \longrightarrow P_1 + P_2(x)$$

A familiar example is that in which P_2, a solid phase (precipitate) containing the desired constituent, is separated by filtration from the solution with which it was in contact.

Separation through Phase Formation. This type of separation may be characterized by the equation

$$P_1(x) \longrightarrow P_2(x) + P_3$$

where the essential operation involves the transformation or production of a new phase—i.e., the emergence of a phase from a persisting or existing phase—followed by mechanical separation of the phases. This type of separation is exemplified by such well known processes as precipitation and crystallization, electrodeposition, and volatilization and condensation. An outstanding example of the latter type of operation is the use of fractional distillation or rectification in separating organic compounds.

Separation by Transference between Phases. Schematically, the operation is represented by the equation

$$P_1(x) + P_2 \longrightarrow P_1 + P_2(x)$$

In the presence of a phase containing the desired constituent, x, a new phase is introduced; competition occurs between the two phases for the desired component, resulting eventually in the more or less complete transfer of x to the new phase; the final operation usually involves the mechanical operation of the phases. This type of operation includes all partition-distribution (phase-equilibration) processes which are summarized in Table I.

Table I. Partition-Distribution Processes

Phases in Contact			
Original	Added	Typical Technique	Example
G	G	...	None
L	G	Evaporation	Drying in air stream
S	G	Evaporation	Drying in air stream
G	L	Absorption	Orsat gas analysis
L	L	Extraction	Organic separations
S	L	Dissolution	Soxhlet processes
G	S	Adsorption	Turner-Burrell apparatus
L	S	Adsorption	Chromatography
S	S	...	None

MEASUREMENT

The desired constituent may be actually measured by any one of three general types of methods. These types are based upon the possibilities that the measurement may be (*a*) independent or dependent on the amount of material present and (*b*) independent or a function of the nature of the substance being measured. Accordingly, one may have methods which are dependent only on the amount or only on the nature of the material being measured, or which depend both upon the amount and upon the nature of the material being present. This basis of classification is outlined and exemplified in Table II.

Table II. Methods of Measurement

Method Is Function of:			
Amount of material	Type of material	Type of method	Example
X		Nondiscriminatory	Balance
X	X	Semidiscriminatory	Density
	X	Discriminatory	Polarography

Let us consider now the nature of three types of measurement with particular reference to the situations in which they can be used, and to their advantages and limitations.

Nondiscriminatory Methods. Nondiscriminatory methods of measurement are essentially quantitative in nature. Thus, the analytical balance measures mass while the graduated cylinder

measures volume, without any particular reference to the nature of the substance whose mass or volume is being measured. The technique involved in such measurements is relatively simple. They have the advantage of giving directly a value which can be interpreted with a minimum of calculation or previous calibration in terms of the desired result which is usually a concentrationlike value—e.g., per cent by weight or volume, or, less commonly, a statement of the absolute amount present. The serious limitation of the method is its lack of specificity. From the measurement one gains no knowledge regarding the nature of the substance being measured; one merely obtains a numerical value related to amount.

Semidiscriminatory Methods. As contrasted to nondiscriminatory methods, semidiscriminatory methods are essentially qualitative in nature. Measurement is based on the variation in value under specified conditions of a physical constant such as refractive index, electrical and thermal conductance, rotation of the plane of polarized light, dielectric constant, viscosity, magnetic susceptibility, standard potential or ionization constant in chemical reactivity titrimetric analysis, and equilibrium constant in many phase-distribution processes where competition prevails.

Measurement of the physical constants involved can be used for the identification of a pure substance—i.e., of a one-component system. In order to use such physical properties for quantitative measurement, one must deal with what is essentially a two-component system. Because the physical constant evaluated yields only a numerical result, one must make $(N - 1)$ measurements for the analysis of a system containing N components; the needed N^{th} value for setting up the N equations containing N unknowns is furnished by the fact that the sum of the mole-fractions present must equal one or, stated another way, the total percentage composition must total 100%.

It is possible to analyze a multicomponent system for a single component by a single measurement of one physical constant if either of two situations prevails: Only the component being measured may vary with the relative amounts of the other components remaining more or less fixed relative to each other, or the component being measured must have a value of the property being measured which is so far different from the values of that property for the other components that the system can be considered to be essentially a two-component system under the conditions of measurement. An example of the first situation is often encountered in the analysis of gases and permits the determination of the variation in a single component by the measurement of the thermal conductivity of the sample. An example of the second class was encountered in the case of product butadiene, where the refractive index of the conjugated diolefin was so far different from that of the simple olefins and paraffins present that a single measurement sufficed to estimate the per cent purity or the total per cent impurity in butadiene which was of 98% or higher purity. An outstanding example of the unique value of a physical property in the determination of a substance is the Pauling oxygen meter which measures the magnetic susceptibility of gases. Because the only paramagnetic gases besides oxygen are certain nitrogen and chlorine oxides, the instrument can be used for the specific determination of oxygen in complex gaseous mixtures.

Semidiscriminatory methods are finding effective use in measuring the composition of flowing streams of materials, either where only one component is effectively varying or where an over-all property of the system is desired—e.g., pH or hydrogen ion activity.

Discriminatory Methods. Discriminatory methods of measurement are essentially combinations of two types of measurements: qualitative semidiscriminatory values and quantitative nondiscriminatory values. The use of such a method gives a "qual-quant" plot, such as is indicated in terms of coordinates in Figure 1. In analytical distillation, the volumes of the desired constituent are measured at selected boiling points or ranges; in polarography, diffusion currents are measured at selected potential values; in *spectrophotometry the per cent transmittance* is measured at selected wave lengths. Discriminatory methods of measurement offer great possibilities in terms of multicomponent analysis, either of the type where different components are measured successively as in polarography or where the N components of a sample may all be determined by making N measurements on the composite pattern obtained as in infrared spectrophotometry. The use of a discriminatory technique of measurement at one fixed qualitative value converts it into a semidiscriminatory technique.

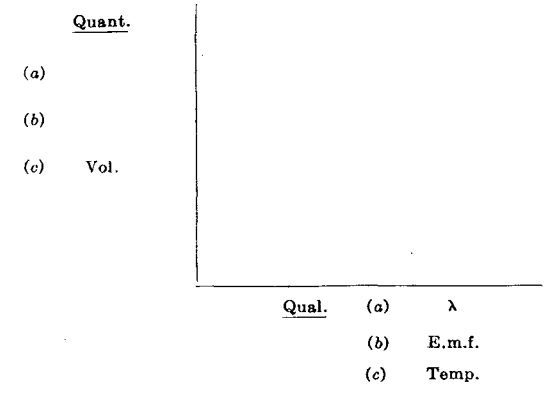

Figure 1. Discriminatory Measurements

The field of the discriminatory methods offers great possibilities for both present and future development. In particular, there is need for refining our techniques so that we can make our quantitative measurement within a more narrow range of qualitative spread, such as the measurement of per cent transmittance in narrower wave-length regions—i.e., the use of smaller spectral band widths.

As an example of the development towards discrimination, one may consider the trend in photometric methods toward improved methods for measuring the per cent of radiant energy transmitted—i.e., improvement of the quantitative factor, and the utilization of more narrow spectral band widths in order to improve the selectivity—i.e., qualitative factor—of the technique. Starting out with the visual comparator using a set of Nessler tubes or its equivalent and visual inspection, one can improve the measurement of the per cent transmittance by using a Duboscq colorimeter. Still more precise measurement of the transmittance as well as greater selectivity of absorption can be achieved in the use of a filter photometer, using a photoreceptor. From the latter instrument it is logical to progress to the still more selective spectrophotometer. Having achieved improvement in both the qualitative and quantitative factors, the next step is the automatic recording of the data, as in the recording spectrophotometer which measures the variation in transmittance with time at one wave-length region or in the scanning spectrophotometer which produces the familiar "qual-quant" record for a single sample. The final development is the application of the response of the photometric instrument to the automatic control of a chemical process.

Measurement Techniques. In most of the semidiscriminatory and discriminatory methods of analysis we do not measure directly the two prime types of data which the analyst requires—i.e., mass or concentration. Instead, in these so-called "physical methods of analysis," we obtain a certain numerical value for a physical property which must then be correlated with either mass or concentration. It is usually more convenient to obtain a correlation with the latter.

Most, if not all, of the physical methods of analysis use one or more of the following four types of methods to obtain the corre-

lation between the measured value and concentration. It is significant that the application of almost any physical measurement to determining quantitative composition progresses through part or all of these four types of calibration in the order listed.

STANDARD SERIES METHOD. In the standard series method which is probably the most fundamental method of calibrating analytical techniques, one compares the value obtained by the particular technique used to the values obtained for a series of samples containing varying but known amounts of the desired constituent. Usually one series of known samples is analyzed to obtain a calibration curve, which is then used to estimate concentration from the measured property. This approach presupposes that the essential experimental conditions are identical during calibration and analysis.

In one modification which may compensate for variation in certain experimental conditions, a known standard is measured with each batch of unknown samples and the data obtained are handled by proportionation to determine the composition of the sample; this modification presupposes that the relation between measured property and composition is linear in the range covered.

ADDITIVE METHOD. The additive method assumes that over a relatively short range of concentration of the constituent being measured, there is a linear variation between the amount of the desired constituent and the effect which is being noted. In this method a measurement is made on the sample, a known amount of the desired constituent is added to the sample, the modified sample is remeasured, and the amount of the constituent originally present is then determined by proportionation. This method requires a standardization run for every sample, but does compensate for the effect of many environmental conditions and may compensate for a proportional variation in the relation of the property measured and the composition caused by the nature of the sample itself.

INTERNAL STANDARD METHOD. In the internal standard method the behavior of the desired constituent is compared to that of a component which is either present in known amount or added in known amount. Examples of this technique are the homologous pair technique of emission spectroscopy and the pilot ion technique used in polarography. The principal advantage of the internal standard technique is that it provides compensation for varying environmental factors which may affect the relative magnitudes of the physical measurements being made. In addition, the method affords an easy way of determining relatively unstable substances for which the use of the standard series method or the additive technique would not be feasible. Essentially the internal standard method operates as follows. Values are measured for the constituent being determined and for the internal standard component. The ratio of these measurements is then compared to a calibration chart of different ratios versus the concentration of the desired component. The principal requisite in the use of this method is to find a standard component whose variability in reference to the measured property is the same as that of the desired constituent for the significant environmental factors.

USE OF FUNDAMENTAL RELATION. Calculation of the amount or concentration of x, using a basic equation which relates the concentration of the desired constituent to the measured property, is gradually increasing in importance. An example is the use of the Ilkovič equation in polarography to calculate concentration from the measured diffusion current. Similarly, Beer's law is used in photometric measurements. This technique involves knowledge of the values, under the experimental conditions, of all the terms included in the equation.

In all or almost all of the so-called physical methods of analysis, it is apparent that before making analytical measurements one must have pure samples of the constituents to be determined, and, often, working curves must be prepared relating the concentration of the desired constituent to the property being measured.

It is true of any analytical method based on a physical property that the reliability of the method is ensured by the constant activity of that property which is measured. This constancy is customarily achieved by control of the variables affecting that property or by appropriate correction for the effect of the variables on the property. For example, in the infrared spectrophotometric analysis of gaseous mixtures, variables such as the pressure and temperature of the gas, and the wave-length region and distribution of the radiant energy to be absorbed are readily corrected for or controlled; there is no control, however, over the specific effects of the diluent components upon the absorption of the principal absorber and the variation in magnitude of these effects with variation in the composition of the mixture. In situations where pressure broadening phenomena in the case of the principal absorber are significant, ability to correct for the effect of the diluent components will control the applicability of the analytical method.

CALCULATION AND INTERPRETATION

The fourth and final stage in the analytical process is the one that is often rapidly disposed of. The calculation and interpretation of the numerical data obtained are a vital link in the analytical process. Because analytical measurements are made to provide certain desired information, it is essential that the analytical data be expressed in the form that will be most helpful to those who are to use the analytical results.

From the mechanical standpoint there have been a number of innovations in recent years. Calculators employing the approximation technique have been of the greatest service in enabling multicomponent analysis of mixtures to be completed in a reasonable period of time. These calculators or computers have found widespread application in infrared absorption spectrophotometry and in mass spectrometry.

One of the most significant developments of the past decade in analytical chemistry is undoubtedly the greater attention paid to statistical techniques both in the development of analytical procedures and in assaying the value of analytical data. Increasingly greater use is being made of indexes of precision. The analytical chemist should undertake to evaluate his results in reference to confidence limits. We all know that the analytical results may be incorrect; it would be of great value to know what chance is being taken that the analytical results presented are incorrect—i.e., that they are actually beyond a certain range around the reported value. In place of reporting the percentage of x in the sample as 32.3, it is more nearly correct and probably more valuable either to express the result as follows or to have it understood as meaning: "There are 98 chances in 100 that the content of x is in the range of $32.3 \pm 0.3\%$."

The interpretation of analytical data in reference to the purpose for which they are being sought is usually left to the person for whom the data are being obtained. Because the analytical chemist is presumably better aware of the limitations of the separation and measurement processes of the analysis than is the recipient of the analytical results, the analytical chemist should attempt to aid in the interpretation of the analytical data, particularly in the case of complex mixtures whose composition may not be fully known.

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Classification of Methods of Quantitative Analysis

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Representative existing classifications of analytical chemical methods are critically surveyed on the basis of several fundamental criteria. The basic difficulty is shown to be confusion of definitions of the various operations. An improved classification is presented which generally satisfies the fundamental criteria for a satisfactory system, eliminates most of the difficulties inherent in present systems, and is capable of serving as the basis of an improved indexing system.

AS STUDENTS and later as teachers, the authors have observed that after an elementary course in quantitative analysis the student gets the impression that quantitative analysis consists of gravimetric and titrimetric methods. He may have been introduced to colorimetry. Then, in an advanced analytical course or in a physical chemistry laboratory he is suddenly confronted with many new and diverse methods, used infrequently in some cases, but essential in specific applications. If he has occasion to make up a list of all known methods, the array becomes bewildering. The following partial list is an illustration:

Absorption spectrometry
Absorption spectrography
Amperometric titrimetry
Biological assay
Capillary analysis
Colorimetry
Combustion analysis
Conductometric titrimetry
Coulometric analysis
Critical solution temperature method
Densitometry
Electrical conductivity method
Electrodeposition
Electrographic analysis
Emission flame spectrophotometry
Emission spectrography
Fluorometry
Gas analysis
Gravimetric analysis
Magnetic susceptibility methods
Mass spectrography
Mass spectrometry
Melting point and freezing point change method
Microscopical analysis
Nephelometry
Neutron capture
Polarimetry
Polarography
Potentiometric titrimetry
Raman spectrography
Refractometry
Sonic methods
Spectrophotometry
Thermal conductivity method
Titrimetry
Turbidimetry
Viscometry
Volume of liquid distilled
Volume of precipitate
X-ray diffraction analysis
Zymometry

The student is likely to ask himself, "Will they ever end?" When assembled they are still just a list without order, rhyme, or reason. Enumeration of the names gives no suggestion of where an opportunity exists for devising a new method.

On the other hand, classification gives boundaries to the field and order to the list. Presented thus to students, the methods seem connected and are more easily remembered. Furthermore, the structure of the pattern may suggest possible new methods. Finally, if the classification has functional foundation, it may be used as the basis of an indexing system.

CRITICAL SUMMARY OF PRESENT CLASSIFICATIONS

Before examining the virtues and faults of the various classifications which have appeared in the literature, it would be well to list the requisites of an ideal classification. Cohen and Nagel (*4*) give three general requirements as:

1. A division must be exhaustive
2. The constituent species of the genus must exclude one another
3. A division must proceed at every stage upon one principle, the *fundamentum divisionis*

To these basic requirements it seems necessary to add several specific requirements for an ideal classification of analytical methods:

4. It must be based upon the generally accepted divisions of chemistry and physics
5. It must use a generally accepted vocabulary
6. It must be of definite utility
7. It must not involve theoretical knowledge on a level above that of an undergraduate in chemistry
8. The criteria for differentiation must be simply and clearly defined
9. It must be capable of expansion and intensification without the necessity for radical revision

Any actual classification will almost inevitably violate to some extent any one or several of the above criteria. This does not in any way decrease their utility as a guide in the formulation of a classification.

The most frequent fault with the classifications which have previously been given lies in the careless use of the word "physicochemical." Willard and Furman (*10*), for instance, cite the measurement of specific gravity as an example of a physicochemical method. If a hydrometer is placed directly in a solution that is to be analyzed, the method is purely physical. If some chemical preparation of the sample is required, these authors do not consider this as part of the method to be applied and subsequent measurement of specific gravity still involves a physical property only. But according to its definition, physicochemical should involve the principles of both physics and chemistry, which makes this term inapplicable here. If preparation of sample is to be included as part of the method, then this method would be physical in certain cases and physicochemical in others.

Furthermore, the inclusion by these authors of preliminary treatment of the dissolved sample (prior to precipitation) as part of the gravimetric method is not logical. The essential idea of such a method is that the addition of some agent causes a new phase to separate and the addition of this agent is the logicla starting point of the method. Outside of these difficulties, the classification suggested by these authors has much to commend it.

Kolthoff and Sandell (*6*) do not make an attempt at classification and their list of "physicochemical" methods is just that, merely a list. They are definitely in error in describing density, refractive index, and color as physicochemical properties. Kolthoff and Sandell, furthermore, use "specific" to denote a property possessed only by the substance in question, such as its emission spectrum. They refer to properties possessed by all specimens of matter but differing in magnitude as "unspecific" properties—e.g., density, refractive index. In addition, they recognize that some properties are both "specific" and "unspecific"—e.g., conductivity of electrolytes, optical activity of certain compounds.

Patterson and Mellon (*8*) classify properties according to an original concept of "static" and "dynamic" properties, a static property being a contained property of the system, while dynamic properties are those which require transmission or emission of wave motion for their measurement. "Waves" are interpreted to include moving particles by the application of de Broglie's equation for a moving particle of mass m and velocity v, $\lambda = h/mv$, where λ is the wave length and h is Planck's constant. In listing properties they advocate revising the spelling of several terms in the interest of consistency and devise other new terms—e.g., "refractimetry," "masspectrimetry," "potentiimetry." In con-

trast to the previously cited authors, they name methods wholly on the basis of the property used in the final measurement and consider the "separation of the desired constituent" extraneous to the method. Taking what we now call ordinary gravimetric analysis as an example, this would mean presumably that, because the measurement is one of mass, the operations of precipitation, filtration, etc., are not to be considered as part of the "method." Because the term "gravimetric analysis," as now used, includes these operations as essential parts of the method, it would have to be redefined or replaced. Such a step is in opposition to the requirement that a desirable classification use a generally accepted vocabulary. The same may be said with regard to their extensive terminology revisions and additions.

Another objection to the classification of Patterson and Mellon is on the basis of requirement 7, that the necessary knowledge involved be on an undergraduate level. This is definitely not true of the concepts involved in de Broglie's equation.

The size of the sample used for analysis has been an important aspect of analytical methods since the founding of microchemistry by Emich (*5*), who speaks of milligram and centigram methods. The divisions into macro, semimicro, and micromethods are rather indefinite, and, according to various authors, involve, respectively, samples in the ranges 100 mg. and above, 50 to 80 mg., and 15 to 1 mg. or less. The scale of sample size is an important consideration and usually requires modification of the technique involved in work on a different scale. At times, such a classification would be useful but, in general, its importance would be secondary to the identification of the method, especially as most methods can be adapted to different scales of sample sizes.

Another basis of classification has recently come into general use—namely, instrumental and noninstrumental methods. Many colleges and universities now offer courses in instrumental analysis. At least one text (*11*) for such a course has been written and others are known to be planned. Although this classification has fairly wide usage, several authors (*7–9*) have pointed out the ambiguity of the term "instrumental." Manual and semiautomatic might be somewhat better. Whatever the name, the classification is needed and used, though it does not satisfy the requirement that the criteria for the differentiation of methods be clearly definable.

Celsi has given considerable attention to the classification of analytical methods (*1–3*). His divisions (*3*) of physical, chemical, and biological methods are the ones advocated in the present paper, but his over-all title of "Methods of Quantitative Chemical Analysis" reflects the common confusion over sample preparation, which may be chemical, and the method of analysis, which may be purely physical. His subdivision of chemical methods according to whether measurement is carried out upon a reagent or a product (he proposes the terms "reactivimetría" and "corisimetría," the latter from the greek χωρισισ, "separation") is a logical one, but as he admits, fails to provide a satisfactory niche for the method of gas analysis. His alternative basis, the physical state of the sample, does not appear to fulfill the requirement that a classification have definite utility.

DEVELOPMENT OF A SATISFACTORY CLASSIFICATION

The scientific utility of a classification rests upon its defined basis of systematization. The choice of this foundation, then, is the first and most significant step in the development of an acceptable classification. The basis for the classification presented here is operational—that is, the classification is based upon the fundamental nature of the operations which are carried out upon the material to be analyzed. The purpose in using an operational (or functional) basis is to clarify the fundamental nature of the operation itself, inasmuch as this is the source of confusion in the organization of the science of analytical chemistry.

Differentiation between preparational operations and measurement operations must next be established. In this paper a "method of analysis" is defined as a procedure or sequence of operations which makes possible a quantitative estimation of the chemical composition of any material. "Determination" denotes an operation which involves a measurement, while "preparation" denotes any operation to which the material must be subjected before a measurement can be applied.

Thus, the basic structure of the proposed classification is:

Classification of Quantitative Analytical Methods

1. Methods of Preparation of Sample
2. Methods of Determination of Desired Constituent

It is recognized that practically all preparational operations can be differentiated on the basis of their being either essentially physical or essentially chemical. Although the differentiation between chemistry and physics is, on a fundamental scientific basis, arbitrary, such differentiation is pedagogically justified on purely traditional considerations. The distinction between a chemical process and a physical process is made by considering whether or not the chemical composition of the system changes as a result of the process. Although it is realized that this is a cyclic definition, the traditional acceptance of the idea of a chemical change, it is felt, validates its use. The development of division 1 is simple and direct, requiring no further discussion at this point.

Because of the enormous number of methods of measurement available to the analytical chemist, the classification of these methods, in order to be useful, must achieve a high degree of differentiation. The primary classification basis is not so simple as in division 1, for biological methods of measurement comprise a significantly large subdivision. Two questions are asked:

1. Is the determination based primarily on the response of a living organism?
2. If not, does the chemical composition of the system change as a necessary result of the determination?

From the answers to these questions it can be decided whether a given determination is biological, chemical, or physical. In a similar manner, other questions are asked until the system is sufficiently extended to differentiate satisfactorily between the currently available methods of determination. As new methods become available further extension may become necessary. Because the entire classification is given below and the various criteria which are its basis are either presented therewith or are "dictionary" definitions, it would be redundant to repeat here the actual questions used in the development.

The use of a decimal symbology for denoting the various divisions is made in anticipation of subsequent applications of the classification to an indexing system in which such a symbology has definite and obvious conveniences.

Classification of Quantitative Analytical Methods

1. Preparation of Sample (operations necessary to permit measurement)

.1—Physical (chemical composition of system does not change as a result of the operation)

.01—Sampling
.02—Examination
.03—Division
.04—Size separation
.05—Drying
.06—Conversion to desired state

.001—Dissolution
.002—Crystallization
.003—Filtration
.004—Extraction
.005—Physical adsorption
.006—Distillation
.007—Fusion

.2—Chemical (chemical composition of system changes as a result of the operation)

.01—Examination
.02—Conversion of system to desired chemical composition

2. Determination of Desired Constituent (operations involving measurement)

.1—Biological (based primarily upon response of living organism)

.01—Microbiological

.001—Antibacterial methods
.002—Growth stimulation methods

.0001—Population methods
.0002—Chemical growth product determinations

.02—Macrobiological

.001—Physiological methods
.002—Psychological methods

.2—Chemical (chemical composition of system changes as a result of determination)

.01—Spontaneous decomposition. Loss in mass measured (ignition methods)

.02—Reaction incomplete. Concentration measured.

.001—Diffusion current measured (polarography)
.002—Reaction rate measured (kinetic methods)

.03—Stoichiometric quantity of reagent added and end point determined by indicator. Measurement by quantity of reagent used.

.001—Reagent is a liquid (titrimetry)

.0001—Chemical indicator

.00001—Self-indicator
.00002—Added
.00003—External

.0002—Physical indicator
.00001—Potentiometric
.00002—Conductometric
.00003—Amperometric

.002—Reagent is an electric current (coulometric analysis)

.04—Excess reagent added

.001—Mass of product measured (gravimetric analysis)

.0001—Chemical precipitation
.0002—Electrodeposition
.0003—Gas evolution and absorption

.002—Volume measured

.0001—Volume change of reaction mixture measured (gas analysis)
.0002—Volume of product measured
.00001—Solid (volume of precipitate methods)
.00002—Gas (evolution methods)

.3—Physical (chemical composition of system does not change as a result of determination)

.01—Optical

.001—Absorption
.002—Emission
.003—Scattering
.004—Diffraction
.005—Refraction
.006—Interference
.007—Polarization
.008—Reflection
.009—Combinations of above

.0001—X-ray
.0002—Ultraviolet
.0003—Visible
.0004—Infrared
.0005—Microwave

.02—Electrical

.001—Electromotive force
.002—Conductivity
.003—Current
.004—Inductance
.005—Dielectric constant

.03—Magnetic

.001—Susceptibility
.002—Permeability
.003—Saturability

.04—Acoustical

.001—Absorption
.002—Interference

.05—Mechanical

.001—Hardness
.002—Tensile strength
.003—Elasticity
.004—Density
.005—Length, area, or volume
.006—Viscosity
.007—Interfacial tension

.06—Thermal

.001—Phase change temperature
.002—Calorimetry
.003—Diffusivity
.004—Conductivity

.07—Elementary particle

.001—Ions
.002—Electrons
.003—Protons
.004—Neutrons
.005—Other particles

.0001—Absorption
.0002—Emission
.0003—Scattering
.0004—Diffraction
.0005—Refraction
.0006—Combination of above

DISCUSSION OF UTILITY AND APPLICABILITY

Before applying the system to specific cases, several important features should be pointed out. Gravimetric analysis is considered to consist of the chemical separation of a phase by addition of a reagent, followed by measurement of the mass of the separated phase. Chromatographic "analysis" is a method of preparation of sample, because it is a technique of separation only. (The term "chromatography" is to be preferred.) In classifying so-called electrochemical methods of analysis, distinction is made between those that merely involve electrical indication of titration end points and complete analytical methods such as polarography and electrodeposition.

In order to check the applicability of the classification, a copy of *Chemical Abstracts* was chosen at random from the current volume. In the Analytical Chemistry section, a pair of adjacent columns was chosen at random by a disinterested observer. The reference selected was *Chem. Abs.*, **43**, 5701–2 (1949). All the references in these columns were successfully differentiated, using the above classification. Although this admittedly was not a satisfactory test to which to subject the system, it was felt that it offered at least a preliminary estimation of the applicability of the scheme. The papers are listed below by page reference and title only and are followed by the appropriate classification index number:

5701*a*—Diagram for the analysis of potash feldspar on the five-axis universal stage—2.319
5701*b*—The cobalt chloride method for determining combined water—2.23112
5701*c*—A complementing reaction for the identification of hydrocyanic acid by sodium picrate paper—1.21
5701*d*—Polarographic study of molybdiphosphoric and molybdisilicic acids—2.221
5701*e*—Spectrophotometric determination of pH by means of mixed indicators—2.3113
5701*g*—Determination of cobaltammine ammonia. Application to determination of ferrocyanide ion—2.2411; 2.2421
5701*h*—Sensitive test for mercury ion—1.21
5701*i*—Detection of silver and mercury ions and their quantitative (colorimetric) determination—1.21; 2.3113
5702*b*—Inorganic paper chromatography and detection of cations by fluorescence—1.21
5702*c*—Organic elementary analysis—2.2411
5702*d*—Carbon-hydrogen groups in hydrocarbons. Characterization by 1.10- to 1.25-micron infrared absorption—2.3114
5702*f*—Determination of aliphatic alcohols by oxidation with potassium dichromate in the presence of some organic substances—1.22; 2.231
5702*h*—Polarographic determination of saturated and unsaturated compounds—2.221

Although in its present state the system has only a pedagogic value, it will be shown in a subsequent paper that it can be extended easily into a method which permits an unusually rapid and accurate comparison of analytical methods on the basis of:

1. General theory
2. Characteristics
   - *a.* Rapidity
   - *b.* Accuracy
   - *c.* Sensitivity
   - *d.* Complexity
     1. Mathematical
     2. Operational
   - *e.* Cost
     1. Initial
     2. Operational
3. Applicability

A cross-reference system will be shown to be applicable.

The classification does not obey completely the previously cited rules of Cohen and Nagel. Cohen and Nagel feel that "these rules. . . . are of little help in practice. They express an ideal rather than state a method. Moreover, the ideal is inadequate for a well-developed science; it is more suitable to sciences in their infancy." That analytical chemistry today is not an infant science can be verified by any student or chemist who has ever been exposed to the myriads of methods which lie between "absorption spectrophotometry" and "zymometry."

ACKNOWLEDGMENT

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A Cathode-Ray Polarograph

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An improved cathode-ray polarograph, designed around readily available components, is presented with some experimental results obtainable with it. The circuit of the instrument contains a sweep generator capable of applying to the dropping mercury electrode a linear voltage sweep which is continuous from +0.50 through 0 to −2.50 volts, a voltage clipper which prevents the application of damaging excessive voltages to the dropping electrode, a blanking relay which prevents the focusing of the electron beam at the cathode-ray tube screen except when the input voltages are applied to the deflection plates, and a voltage-compensating circuit which maintains the potential drop across the polarographic cell independent of the drop across the series resistor. There is also a built-in vacuum tube voltmeter for adjusting the minimum and maximum values of the sweep voltage. The instrument can be used as a qualitative and quantitative analytical tool, for both inorganic systems and many organic systems. In addition, it is capable of following rapid, as well as slow, reactions of zero, first, and second order. There is no reason to doubt that the instrument is capable of following third-order reactions as well. The real potentialities of this instrument lie in its ability to follow and measure the rates of rapid reactions.

DURING the past decade there have appeared in various journals a few articles on the application of the cathode-ray tube and the oscillograph to polarography (*1*, *2*, *4*, *6*, *7*, *9*). Two basic techniques were developed, one employing a streaming mercury electrode across which is continuously applied an alternating voltage of conventional wave form and frequency—i.e., 50 to 60 cp.—the other employing a dropping mercury electrode across which is applied, intermittently at the proper time interval, a drop-synchronized, linear voltage sweep of short duration (0.1 to 0.5 second). This relatively rapid sweep is applied to the electrode near the end of the drop growth. In both techniques a cathode-ray tube is used in the presentation of the polarographic data obtained. The first of these techniques is ably described by Heyrovský and Foretj (*4*) and the second by Randles (*9*).

From an analytical point of view, the second of these methods showed the better promise of further development into a reliable, generally applicable, quantitative as well as qualitative tool. Indeed, Randles (*9*) described an instrument with which he obtained many useful data of a precision great enough to render them quantitatively significant. All the work reported on in this paper, however, was concerned with inorganic systems, and dealt chiefly with the detection and measurement of the metal constituents of a solution. This is perhaps unfortunate, for it may leave the impression that this instrument is limited to the analysis of inorganic systems. The authors have shown, on the other hand, that it is equally applicable to many organic systems. In fact, it is entirely possible that the real contributions of such instruments will be made in the organic field and in the study of reaction rates.

This paper presents an instrument for use with the second of the above-outlined techniques, which improves upon some of the shortcomings of similar instruments previously reported; offers a circuit design built around components, particularly vacuum tubes, readily available in this country; indicates the value of the technique in organic as well as inorganic analysis; and, finally, demonstrates the potentialities of the device in the realm of reaction kinetics study.

THE INSTRUMENT AND ITS DESIGN

The basic layout of the instrument is depicted in the block diagram of Figure 1. From this it can be seen that the completed de-

vice consists of thirteen interrelated units, which, when caused to operate in the proper sequence, present a cathode-ray picture of the current-voltage curve of the electrode reactions occurring at the surface of the dropping mercury electrode in a polarographic cell. Accordingly, this apparatus is called a cathode-ray polarograph. [The name "oscillographic polarograph" is more appropriately given by Heyrovský (4) to an instrument based on the first of the techniques discussed above, where an alternating voltage is continuously applied to the electrode.] The complete cycle of events that take place in the instrument is as follows:

(1) When a drop falls from the capillary orifice of the dropping electrode there is a sudden large change in the amount of current flowing through the polarographic cell; (2) this current, in flowing through an external series resistance, causes a corresponding sudden drop in potential across this resistor which is applied through the vertical amplifier to the delay gate circuit; (3) this activates the blanking relay and, after a certain time delay, the sweep generator which (4) applies a linear voltage sweep to the dropping electrode after being clipped and acted upon by the compensator; (5) the compensator maintains the linearity of the sweep across the polarographic cell, and causes it to be independent of the series resistor. Next, (6), the change in current manifested by a proportionate potential drop across the series resistor and the linear voltage sweep across the polarographic cell are amplified, and (7) the amplified signals are placed on the vertical and horizontal deflection plates of a cathode-ray tube, respectively, resulting in the desired current-voltage curve of the electrolytic polarographic reactions occurring at the electrode surface in the cell.

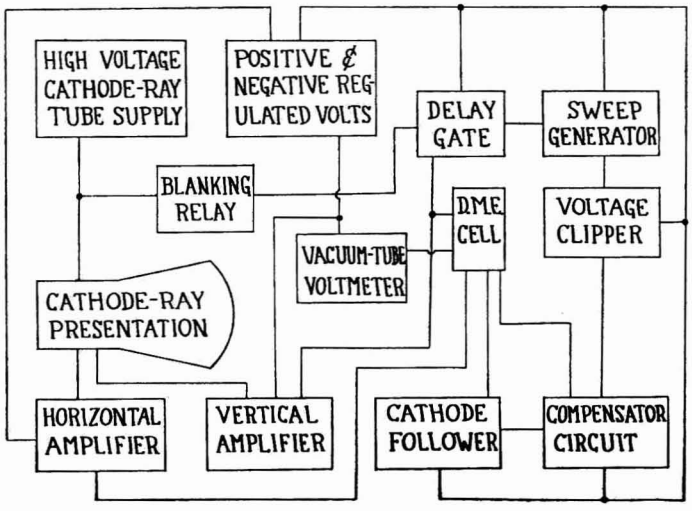

Figure 1. Schematic Block Diagram of Cathode-Ray Polarograph

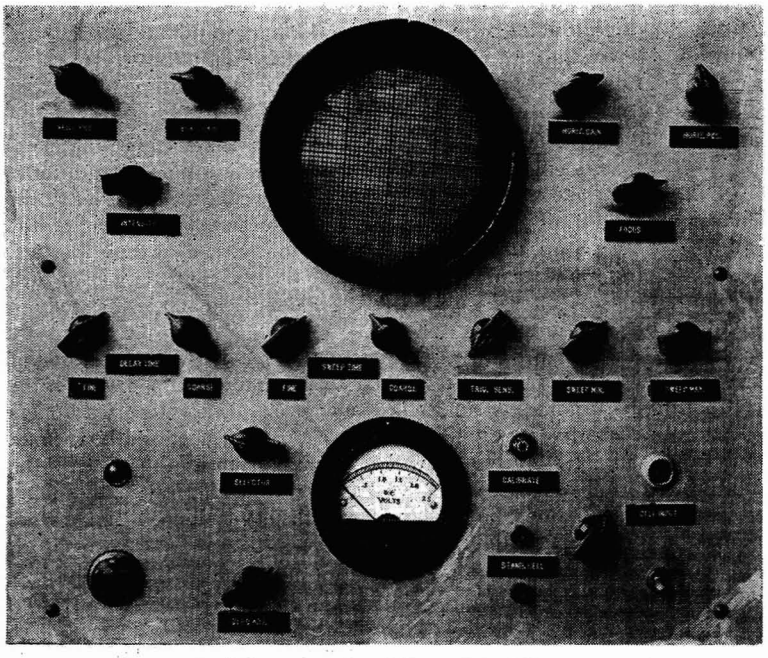

Figure 2. Photograph of Completed Instrument

To enable the curve to persist for a length of time sufficient for proper observation or for photographing, a cathode-ray tube with a long-persistence screen was employed. The vacuum tube voltmeter is built in to facilitate the presetting of the maximum and minimum values of the sweep voltage.

Figure 2 shows the details of the control panel. When the instrument is in use a viewing shield is placed over the cathode-ray screen (not shown in the photograph). The power supplies are in a cabinet separate from the remainder of the apparatus to facilitate maintenance and to eliminate the problems of magnetically shielding the cathode-ray tube from the power sources. In Figure 3 is depicted the polarographic cell assembly, with which a calomel half-cell is used as a reference. This assembly permits a wide choice in the selection of drop time.

Design and Functions of Individual Units. The power requirements for the instrument are not particularly unusual or rigid, but they are specific enough so that no readily available commercial unit will completely suffice. For this reason it was decided to build a power supply and, by so doing, obtain a compact unit designed for the specific purpose at hand. The total power requirements are as follows: −1050 volts rated at 2 mils, +300 volts rated at 90 mils, and +150 and −150 volts, both with a rating of about 30 mils. The last three of these voltages must be well regulated.

The high voltage is used for the cathode-ray tube accelerating potentials, and accordingly need not be electronically regulated. As a result, the high voltage power supply shown in Figure 4 is conventional. (For the component values and ratings, see the complete list of parts, Figure 13.) Smoothing of the raw direct current from the 2X2 rectifier is accomplished with a simple R-C filter, and the various voltages required for the cathode-ray tube are obtained from a bleeder placed across the filtered direct current; the resistance values for this bleeder were calculated in the usual manner. Two of these resistors were made variable in order that they might be used as the intensity and focus controls of the cathode-ray tube. These two controls can be seen on the panel in Figure 2. The condensers, C_1 and C_2, are only 0.1 μfd., which may seem small, but they provide sufficient filtering in this application. The primary consideration here is the high breakdown requirement of the capacitors.

The regulated supply of Figure 5 provides the other three voltages for the circuit. The +300 volts are electronically regulated by the tier of four tubes at the right of the diagram. The +150 and −150 volts are regulated only by voltage regulator tubes (V.R. regulation). Both types of regulation require good filtering of the raw direct current for optimum results, and it will be noted that an L-C filter is used, as compared to the R-C filter in the high voltage supply. Because the breakdown requirements are much less in this case, filter condensers of higher value are employed, which greatly increases the amount of smoothing in the circuit.

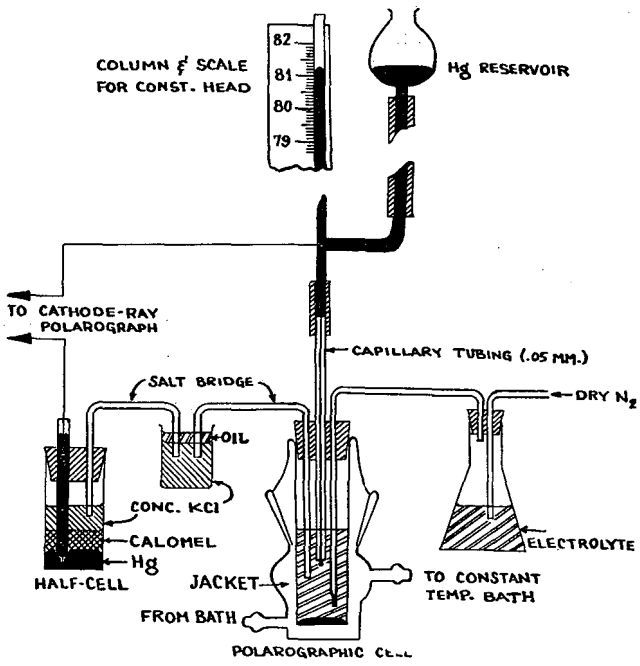

Figure 3. Polarographic Cell Assembly

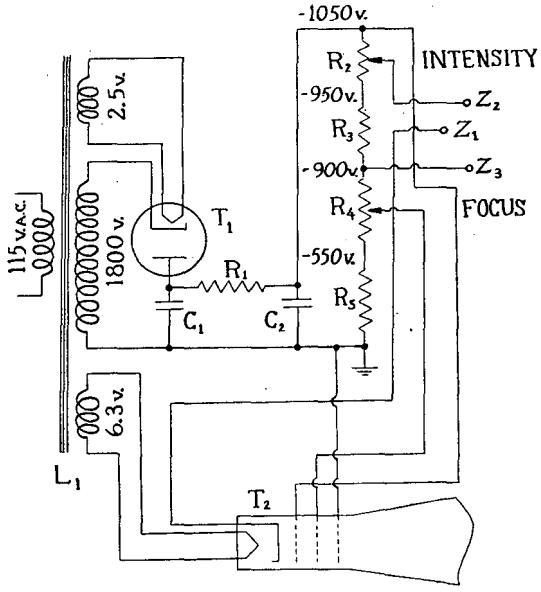

Figure 4. High-Voltage Power Supply

It is necessary for the +300 volts to be highly regulated because of the great stability required in the plate supply voltages for the delay gate, sweep generator, and subsequent stages. If this voltage is not extremely stable, the ripple component appears superimposed on the polarographic curve presented at the cathode-ray tube screen, seriously impairing the usefulness of the curve and the accuracy with which it may be read. This is all the more serious when it is remembered that any ripple component present in the signal before it is amplified will be multiplied by a factor of up to 2000 or more in the vertical amplifier. Considered from another point of view, this problem becomes one of keeping the ripple component level below the point at which it will start to interfere with the direct current signal generated across the resistor in series with the polarographic cell. Because it is desired to detect and accurately measure signals across this resistor as small as 0.005 volt, the ripple component must be kept down to a level equal to 2% of this value. This is not an arbitrary evaluation for the amount of ripple that can be tolerated, as Kolthoff and Lingane (*5*) state that the accuracy of the polarograph under normal circumstances is ±2% in the concentration range from 10^{-4} to 10^{-2} molar. This means that the ripple should not exceed 0.0001 volt in the preamplified signal. This gives a good indication of the amount of filtering and regulation required in the +300-volt source. Two 2A3 power triodes were used in parallel in the output stage of this circuit because of the relatively large (90 mils) load current needs.

DELAY GATE

If any one of the various units of the cathode-ray polarograph can be called the heart of the instrument it is the delay gate, for it is this circuit which synchronizes the voltage sweep across the cell with the drop. In other words, this portion of the instrument ensures that the voltage sweep will occur at the same instant with respect to drop growth for each drop. That this be done is important from two standpoints: (1) to maintain the reproducibility of the curve from one sweep to the next, and (2) to minimize the distortion introduced into the curve by the increase in diffusion current brought about by the increase in the surface area of the drop during the sweep interval.

The necessity of meeting these two conditions can be best realized by considering the current-time curve shown in Figure 6, and by a brief examination of the theoretical equation for the current at any time t (i_t) during the life of a mercury drop. This equation was originally derived by Ilkovič, and a very concise treatment of the derivation and the theory behind it is given by Kolthoff and Lingane (*5*). The equation so derived is

$$i_t = 706\, n\, D^{1/2}\, Cm^{2/3}\, t^{1/6}\, \mu \text{ amp.} \qquad (1)$$

where 706 is a combination of numerical constants, n is the number of electrons involved in the reduction, D is the diffusion coefficient in sq. cm. sec.$^{-1}$, C is the concentration in moles per cc., m is the flow of the mercury in the dropping electrode in grams sec.$^{-1}$, and t is the drop time in seconds.

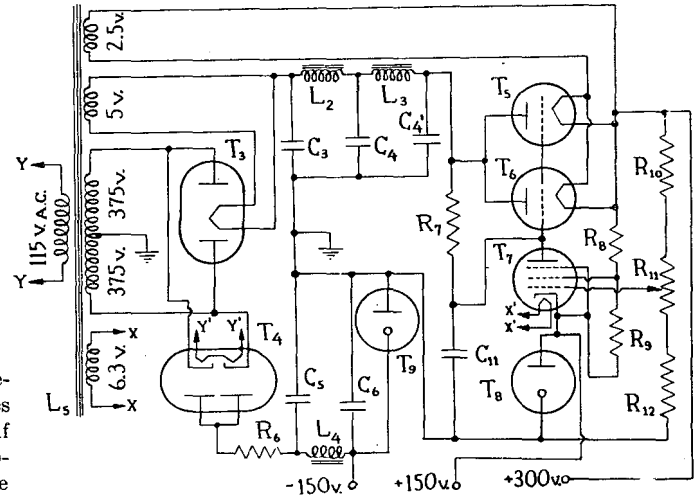

Figure 5. Regulated Voltage Supplies

The curve shown in Figure 6 represents this general Ilkovič equation when concentration C is constant. Because it is obvious that for given cell conditions n, D, and m are also constant, this equation must be a current-time curve, represented by the general form:

$$i_t^{6} = Kt \qquad (2)$$

It can now be observed that unless the voltage sweep across the polarographic cell occurs at the same time, t_1, with respect to the start of drop growth at t_0, the curves appearing at the cathode-ray tube will not be reproducible from sweep to sweep, but will cause the polarographic breaks to vary in amplitude according to the sixth power of the current, i_t, flowing at the time of sweep, t_t.

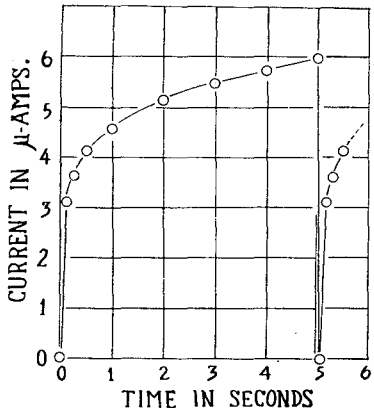

Figure 6. Current-Time Curve for 5-Second Drop Time
$i_t^6 = 9325t$

After this fact has been established, it must be decided next at which point along the curve with respect to time t_0 it is best to apply the sweep each time. This is a problem involving the relationships between the sweep interval and (1) the time which is to elapse from the start of drop growth until the initiation of the sweep, and (2) the total drop time. Because the sweep that is applied to the polarographic cell is finite in value (usually 0.1 to 0.25 second), we must consider the increase in diffusion current during the time of sweep. It is easily seen that any increase in this diffusion current near the end of the sweep will cause a proportionate increase in the amplitude of any ion "break" occurring near the end of the sweep. The same thing is true to a lesser extent of ion breaks occurring at intermediate points during the course of the sweep. The resulting curve will be accordingly distorted. In general, then, for optimum results and minimum distortion the sweep should be applied across the polarographic cell as near the end of the drop as is practicable. If the sweep were instantaneous, it would make no real difference, as far as the introduction of distortion is concerned, where the sweep were applied, but even under these conditions it would be best to choose a point near the end of drop growth, for it is in this region that maximum break amplitude would be obtained for a given concentration.

The only remaining question, now, is the relation of sweep interval to drop time. We must determine what minimum drop time will give satisfactory results. By experiment with the 0.05-mm. capillary tubing used in the dropping mercury electrode, the authors found that the value for K in Equation 2 averaged out to approximately 9325 for such a capillary. This gives, then,

$$i_t^6 = 9325\,t \qquad (3)$$

whose derivative,

$$di_t/dt = 1554/i_t^5 \qquad (4)$$

gives the expression for the rate of change of current with respect to time. If, as previously stated, the accuracy of the polarographic method is $\pm 2\%$, then an increase in diffusion current greater than $0.04\,i_t$, where i_t is the average current during the sweep duration, cannot be tolerated. By substitution in Equations 3 and 4 we find that the minimum acceptable drop time for a sweep of 0.1-second duration is 0.42 second, and for a sweep of 0.2-second duration is 0.85 second. A drop time of slightly more than 1 second is found to be a satisfactory minimum for a sweep of 0.25 second. From other considerations it has been found practical to maintain drop times in the range 3 to 6 seconds, so that in practice the drop times are found to be well above the minimum time required for producing a virtually distortionless curve on the cathode-ray screen, and distortion becomes a problem of minor importance when the sweep is caused to occur at a point approximately 0.5 second from the end of the drop life.

Because the drop time may vary by several per cent from drop to drop, it is perhaps more correct to say that we cause the sweep to occur at a preset time after the beginning of the drop life, rather than at a given time from the end of the drop life. In any event, the pulse received by the amplifier from across the cell series resistor when the drop falls is amplified and fed into the delay gate. The delay-gate circuit is what is commonly called a "one-shot" multivibrator or "flipflop," as opposed to the free-running or continuously oscillating multivibrator. Puckle (*8*) gives a full discussion of multivibrators and circuits of similar type in his excellent book on the subject.

Theoretically, any time delay should be available with such flipflop circuits, but the longer the "leak" time in such a circuit, the less the reproducibility, and, for obvious reasons, the actual practical length of time delay obtainable by this means is dependent on the precision of measurement required. The maximum times in which we are interested do not exceed 5 or 6 seconds, and the reproducibility for times in this range is better than 1%, entirely within the tolerable limits for the cathode-ray polarograph.

The diagram for the delay-gate circuit is presented in Figure 7. The length of the time delay is determined by the size of the leak resistor, a coarse time adjustment being provided by the switch which selects resistors in 10-megohm steps. In series with this switch are a 10-megohm potentiometer and a 2.2-megohm fixed resistor. The variable resistor is used as a fine time-delay adjustment, and the function of the 2.2-megohm resistance is to limit the low end of the times available to some finite value. Thus, the arrangement described permits one to select any resistance value between 2.2 and 32.2 megohms.

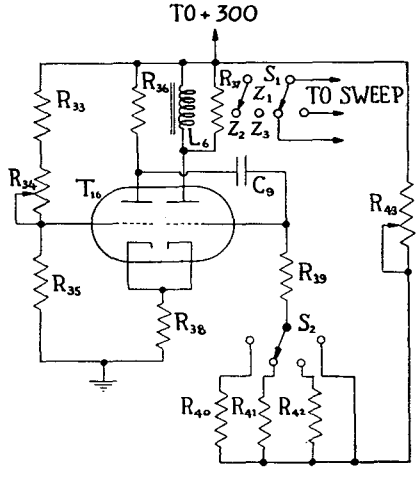

Figure 7. Delay-Gate Circuit

As a plate load for the second stage of the "one-shot" multivibrator included in the delay-gate circuit, we use the coil of a relay, which in turn controls the contacts which operate the voltage sweep generator and the cathode-ray tube blanking voltage. The coil has a direct current resistance of 11,500 ohms, shunted by a 10K resistor, giving an effective load of approximately 5000 ohms. Multiplying this value by 4 (see Puckle *8*) gives the plate load resistance for the first stage, 20,000 ohms.

The function of the potentiometer in the grid circuit of the first stage is for the purpose of adjusting the multivibrator sensitivity—i.e., the magnitude of the triggering pulse required to activate the circuit.

Thus, the operation of the delay gate can be outlined briefly as follows: Stage two is the one normally conducting when a large positive pulse, from the vertical amplifier, is applied to the first grid at the instant the drop falls; this action switches the multivibrator to stage one from stage two, dropping out the relay which is normally closed; and finally, at the end of the time delay, the relay pulls up again as a result of the switchback to the normal multivibrator régime. This activates the sweep generator and "unblanks" the cathode-ray tube. The length of the time delay is set in by means of the time-delay adjustors described, and it will vary, in normal usage, from about 3 to 6 seconds. The delay is fixed at a value approximately 0.5-second less than the average drop time, thus permitting the drop to be nearly full grown before application of the sweep voltage.

SWEEP GENERATOR, VOLTAGE CLIPPER, AND BLANKING RELAY

A diagram of the sweep generator is depicted in Figure 8. Included in this discussion, because of their interrelationship with the sweep generator circuit, are the voltage clipper and the blanking relay. This latter is nothing more than the second set of contacts on the relay controlled by the multivibrator.

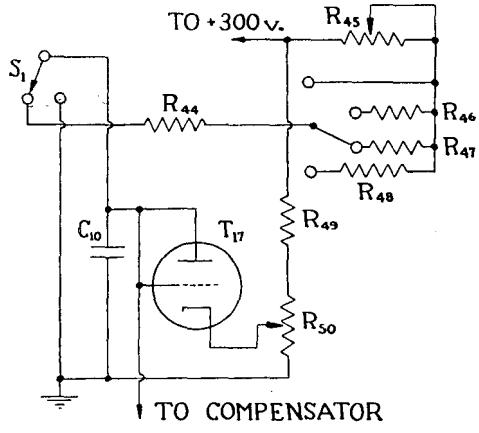

Figure 8. Sweep Generator, Blanking Relay, and Voltage Clipper

The sweep generator in the instrument described by Randles (*9*) starts its sweep at a value of −0.5 volt. Because there are many ions whose half-wave potentials lie in the range 0.0 to −0.5 volt, a sweep generator was designed for use in the authors' instrument which was capable of sweeping from +0.5 through 0 to −2.5 volts. Thus, the range of operation of the cathode-ray polarograph is greatly extended, and the versatility increased. The ability of the instrument to sweep from some small positive potential through zero into the negative range facilitates the investigation of many organic systems where the half-wave potentials may be slightly positive. It was of aid, for instance, in the investigation of gelatin sols.

The sweep generator is basically of the simplest kind, being nothing more than a charging condenser. This condenser, however, is rigidly controlled to prevent the voltage developed across it from becoming excessive. In the diagram the relay contacts are shown in their pulled-up position, which is the case when stage two of the multivibrator is conducting. In this position the charging condenser is connected to +300 volts through a large resistor, the magnitude of which determines the charging rate; the larger the resistor, the slower the charging rate, and the longer it takes the condenser to reach a given value. An examination of the circuit reveals a switching and variable resistor combination similar to the one employed in regulating the delay time. These are the coarse and fine sweep rate adjustments, respectively, providing sweep times of from about 0.1 to 1.0 second. To date, the sweep times most frequently utilized, experimentally, have been in the range 0.2 to 0.5 second. (By sweep time is meant the time required for the voltage across the condenser to reach the maximum value predetermined by the setting on the voltage clipper.)

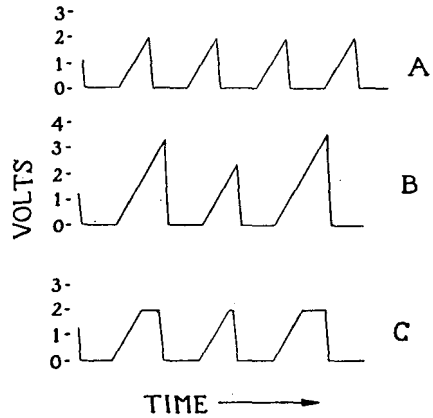

Figure 9. Sweep Generator Wave Forms, Showing Action of Voltage Clipper

A. **Ideal wave form for constant drop time**
B. **Type of wave form actually encountered in practice**
C. **Wave form after addition of voltage clipper**

The primary qualification of this sweep voltage is that it be linear over the range of voltages to be used in the cathode-ray polarograph. The wave form of the voltage developed across a charging condenser is exponential; however, for all practical purposes it is virtually linear at the start of the charging period. The maximum voltage applied to the dropping mercury electrode should never exceed 2.5 volts, less than 1% of the total available charging potential of 300 volts, and consequently the nonlinearity of the sweep so obtained is neither perceptible nor significant in this application.

One of the major failings of previously reported cathode-ray polarograph circuits is the manner by which the voltage sweep is terminated. The method employed was to permit the drop itself to terminate the sweep. Under ideal conditions where the drop rate would be absolutely uniform and perfectly reproducible, this method would perhaps be acceptable, providing one could initiate the sweep at exactly the correct time with respect to the time of drop fall.

Under such ideal conditions, the sweep wave form would be a uniform sawtooth wave, with a delay interposed between cycles. Such a wave form is shown in Figure 9*A*. Unfortunately, the drop times are not exactly reproducible, but vary, even under the best of conditions, by a few tenths of a second. A typical example, obtained experimentally, shows that the drop time was 5.8 ± 0.2 seconds. The wave form of the sweep voltage resulting from such irregularities in drop time is shown in Figure 9*B*. The fact that the wave form itself is not exactly uniform is not particularly serious when considered alone, but the fact that such a situation permits excessive voltage to be applied to the electrode creates considerable havoc. This is especially true at the faster sweep rates, where the voltage increases at a rate of approximately 15 to 20 volts per second. It is a matter of simple arithmetic to see that a variation of ±0.2 second in the drop time can cause a variation in the terminal sweep voltage of as much as 5 volts, if the drop is used as the sweep terminator. In such a case the maximum sweep voltage would lie between 2.0 and 7.0 volts in a normal experiment. (We are considering here the absolute

values of the potentials under discussion. These terminal voltages are actually negative—i.e., the dropping mercury electrode is negative with respect to the pool or some other equivalent point of reference.) That such excessive voltages are extremely undesirable is realized when it is known that voltages as low as 4 or 5 volts cause a pitting and enlargement of the capillary orifice of the electrode, brought about by the fact that the mercury, under the influence of these higher potentials, actually tears away some of the glass from the periphery of the orifice. This effect, moreover, is cumulative, since after a few sweeps the drop size as well as the drop time become very erratic, and much larger on the average. This, in turn, causes still larger terminal sweep potentials, until ultimately this condition proceeds to the point where mercury streams continuously from the electrode in a series of fast drops of irregular size, rendering the instrument completely inoperable.

To correct this condition a voltage clipper was added to the generator circuit. This is simply a diode-connected triode, with cathode bias, placed in parallel with the charging condenser. The potential level of the cathode above ground is determined by the amount of cathode bias set in with the potentiometer, the center tap of which is connected to the cathode. When the charge on the capacitor raises the plate of this clipper to its critical value, this tube begins to conduct, thereby effectively shunting a low resistance across the condenser; the condenser then discharges until the voltage falls below the critical value, and conduction ceases. This sequence of events is very rapid; the whole process is repeated many times a second, having the effect of stopping the condenser charging action at the level of the diode critical value plus the amount of cathode bias. Because the amount of this bias can be varied, the sweep maximum can be adjusted to any reasonable value. By this clipping action, then, we can prevent any excessive voltage from being applied to the electrode regardless of total drop time or any irregularities in this time. A picture of the wave form of the generator output under these conditions, and the one actually encountered in use, is shown in Figure 9*C*.

The second set of contacts on the relay in the multivibrator circuit switches the cathode of the cathode-ray tube to a voltage which prevents the spot from being focused on the screen when the voltage sweeps are not actually being applied to the deflection plates. This prevents the otherwise bright, stationary spot from burning a hole in the cathode-ray tube screen, and facilitates the photographing of the polarographic curves. If the screen is dark, except when the actual curve is being traced, the camera may be opened a second or two before the start of the trace, permitting full utilization of the fluorescence, as well as the residual phosphorescence, of the excited portions of the screen. Before the inclusion of this blanking relay, the camera could not be opened until the sweep had started. By the time the film had been exposed to the rapidly moving spot under these conditions, the spot was anywhere from one third to one half the way across the screen, and the portion of the trace to the left of this point was more dense on the photographic plate than the portion to the right, inasmuch as this latter portion of the curve was burned in by the fluorescence of the moving spot, while the former portion was exposed merely to the residual phosphorescence. This can be seen in the retouched photographs (Figures 14, 15, 18, and 21). For the purpose of initial spot positioning, a blanking relay shorting switch is provided, which eliminates the blanking relay from the circuit.

THE COMPENSATOR

Originally the sweep voltage was applied directly to the dropping mercury electrode through the resistor in series with it. This introduced a rather serious distortion to the polarographic curve, however, because the sweep across the polarographic cell, under these conditions, is linear only if the current through the cell, during the time of the sweep, increases linearly. This is so because, at any instant, the voltage across the cell is equal to the instantaneous sweep voltage less the corresponding potential drop across the series resistor. Also, the current does not increase linearly during the time of sweep, but, rather, it exhibits sudden large increases at the half-wave potentials of the constituent ions present in the cell solution. This caused a marked divergence from linearity of sweep across the cell, inasmuch as a proportionately larger and larger fraction of the total instantaneous voltage was dropped across the series resistor. Because the voltage developed across the polarographic cell was amplified and transferred to the horizontal deflection plates of the cathode-ray tube, this meant that the horizontal, or voltage, axis of the current-voltage curve was not linear with respect to voltage. Thus it was impossible to obtain the half-wave potential of an ion as indicated by a "break" in the curve by simply measuring the displacement from the origin of the break along the x-axis. Furthermore, the nonlinearity of this horizontal sweep is a function of the number of ions present in the cell solution, and of their respective concentrations. The influence of this latter factor—i.e., the dependence on ion concentration—means, specifically, that in a titration where ion concentration is increasing, there is an apparent shifting to the left along the voltage axis of the break due to the presence of the ion whose concentration is increasing. The opposite effect is evident in titrations where the concentration of the given ion is decreasing.

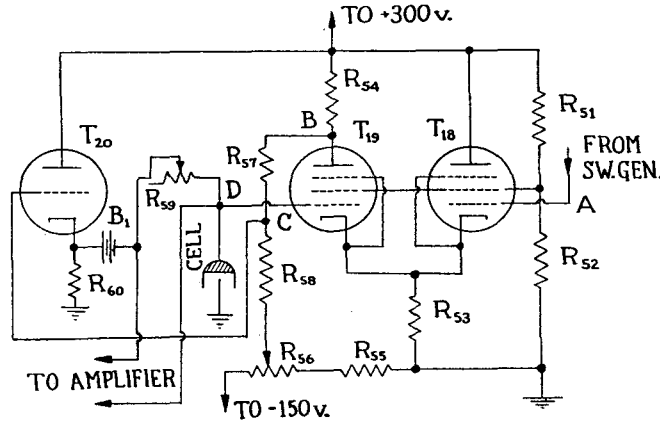

Figure 10. Compensator Circuit

These difficulties were resolved by the development of what may be called the "voltage compensator" circuit, or more briefly, the compensator. Randles (*9*) included as a part of his cathode-ray polarograph a circuit which performs a similar function, although it differs in operational detail from the one here described. A diagram of the circuit discussed here appears in Figure 10. The function of this circuit is to maintain the drop across the polarographic cell independent of the drop across the resistor in series with it.

The action of the circuit is such that if we apply an increase in the voltage at point A, the point of application of the sweep voltage from the generator-clipper circuit, the plate current through the cathode-follower stage increases. This results in a rise in the cathode voltage with respect to ground. This, in turn, increases the bias on the second, or left-hand, stage of the circuit, consequently decreasing the plate current through the pentode. Under ideal conditions the sum of the currents through these two stages will remain constant. This is not entirely true here, however, because of the presence of some degeneration. This, decrease in plate current in the pentode stage causes a corresponding decrease in the potential drop across the 100K plate load resistor, and subsequent rise in the voltage at point B, which, in turn, induces a similar proportional rise at point C. The coupling between point C and the grid of the 6J5 cathode-follower causes this grid to rise in accordance with the change at C. The current through the 6J5 increases as a result of this grid rise, and the resulting increase in the voltage drop across the cathode resistor is

applied to the dropping electrode and its series resistance. The function of the battery, B_1, is to buck out the normal drop across the cathode resistor and to maintain the potential across the cell at zero until the sweep is applied.

When this change in voltage across the cathode resistance is applied to the cell-resistor combination in series there is a rise in voltage at point D. Point D, however, is the grid of the pentode stage of the compensator, and this rise in voltage at D counteracts, in part, the increase in pentode bias caused by the rise in voltage across its cathode resistor. This means that the change in potential at D will not be as large as the corresponding change at A. The important fact is that this arrangement assures that the voltage at D—i.e., across the polarographic cell—will be a faithful, proportionate reproduction of the voltage applied at A if the pentode amplifier is operated on the linear portion of its $i_p - e_g$ characteristic. That this is true is evident from the obvious feedback characteristics of the circuit—i.e., any tendency toward nonlinearity at D is counteracted by an equal, but opposite, effect brought about by the circuit action just described. Thus a linear sweep at A will result in a linear sweep at D. This is demonstrated by the data appearing in Table I.

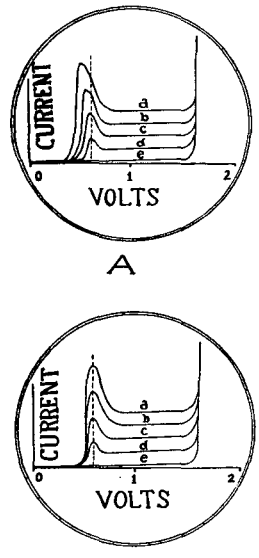

Figure 11. Compensator Action

Leftward shift of Cd^{++} peak with increasing ion concentration (*a*) without compensator, and (*b*) after inclusion of compensator, showing elimination of shift
a. Cd^{++} concn. = 8.0 × 10^{-4} *M*
b. Cd^{++} concn. = 6.0 × 10^{-4} *M*
c. Cd^{++} concn. = 4.0 × 10^{-4} *M*
d. Cd^{++} concn. = 2.0 × 10^{-4} *M*
e. Pure supporting electrolyte, 1 *N* NH_4OH + NH_4^+

The tests resulting in Table I were made with a fixed value of cell resistance. Because the resistance of the cell normally varies considerably during the course of the voltage sweep, it still remained to be demonstrated whether or not the potential across the cell could be caused to remain independent of this resistance change by the circuit described.

Data of a conclusive nature were obtained with a "dummy" cell—a potentiometer that had been substituted for the polarographic cell. The potentiometer used was made variable from 5000 ohms to 45,000 ohms.

The input voltage at A was varied in 0.50-volt steps, which caused proportionate changes at D of 0.28 volt, as seen. The resistance of the dummy was then rapidly varied (simulating a sudden ion break) between values, which caused large deflections on the microammeter which had been placed between the dummy and ground. In all but the first two steps (Table II) the maximum current was limited by the range of the meter used, but this did not matter, because the changes in current through this dummy cell were many times greater than those encountered in actual practice. This was done so that the circuit could be tested under extreme conditions.

Data obtained by the above procedure are shown in Table II. It is clearly indicated, then, that the changes in the voltage across the cell, caused by a rapidly changing cell resistance, are negligible, and that this voltage is therefore independent of such resistance changes, and hence is independent of the flow of current through the cell. Similar tests were made without the inclusion of the compensator circuit; the voltage across the cell was found to vary from 0.2 to 0.8 volt with similar changes in cell resistance. This compares to an average change of only 0.03 volt when the compensator was used.

Table I. Comparison of Voltages at Points A and D of Compensator

Voltage at A	Voltage at D	ΔV at A	ΔV at D
0.00	0.00	...	...
0.50	0.28	0.50	0.28
1.00	0.55	0.50	0.27
1.50	0.83	0.50	0.28
2.00	1.11	0.50	0.28
2.50	1.40	0.50	0.29
3.00	1.68	0.50	0.28

Table II. Measurements Made with Dummy Cell

Voltage at A	Voltage at D	Voltage Change [a]	[b]	i_r, μa.[c]	i_m, μa.[d]	Δi, μa.[e]
0.00	0.00	0.00	0.00	0	0	0
0.50	0.28	0.00	0.02	1	43	42
1.00	0.55	0.00	0.03	2	89	87
1.50	0.83	0.00	0.02	3	>100	>97
2.00	1.11	0.00	0.02	5	>100	>95
2.50	1.40	0.00	0.025	6	>100	>94
3.00	1.68	0.00	0.035	7.5	>100	>92.5
3.32	1.85	0.00	0.04	8	>100	>92

[a] Change in voltage at A as resistance of dummy cell varied from maximum to minimum.
[b] Same for voltage at D, estimated as closely as possible.
[c] i_r, current when resistance of dummy cell was maximum.
[d] i_m, maximum current observed. For first three readings this occurred at minimum resistance. Others were restricted by meter scale.
[e] Change in current through cell from maximum to minimum resistance conditions.

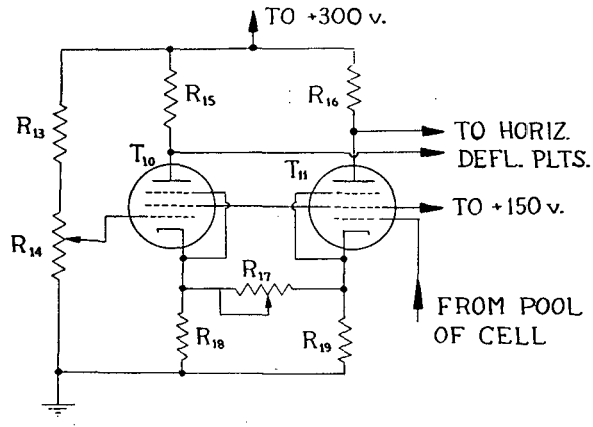

Figure 12. Horizontal Amplifier

It is possible, now, to use the change in voltage across the cell as a reference for the horizontal sweep on the cathode-ray tube, and know that the voltage on this axis is proportional to time and to the displacement along the axis from the origin of the curve under all conditions. Figure 11, A and B, shows the performance of the instrument before and after the inclusion of the compensator circuit. The ion used for this illustration is cadmium in 1 N ammonium hydroxide plus 1 N ammonium ion. The elimination of the shift in the ion break now makes ion identification absolute, and the half-wave potentials may be determined with reasonable accuracy—i.e., within 0.01 volt.

AMPLIFIERS

All the amplifiers employed in the cathode-ray polarograph are direct-coupled or direct current amplifiers. They are of conventional design with no more than the usual attempts at drift elimination, etc., inasmuch as the slight effects of a small amount of drift can be compensated for by an occasional repositioning of the spot on the cathode-ray screen. Actually, after the circuit has been in operation for 2 or 3 hours, the amount of drift is imperceptible over a period of 0.5 hour, and when it is known that the instrument will be used the following day, it is left on during the night.

The vertical amplifier consists of two push-pull stages with an over-all gain of 2400; the horizontal amplifier is a single-stage push-pull amplifier with a gain of 60. Because these amplifying stages are all similar in operation, Figure 12 shows only the single-

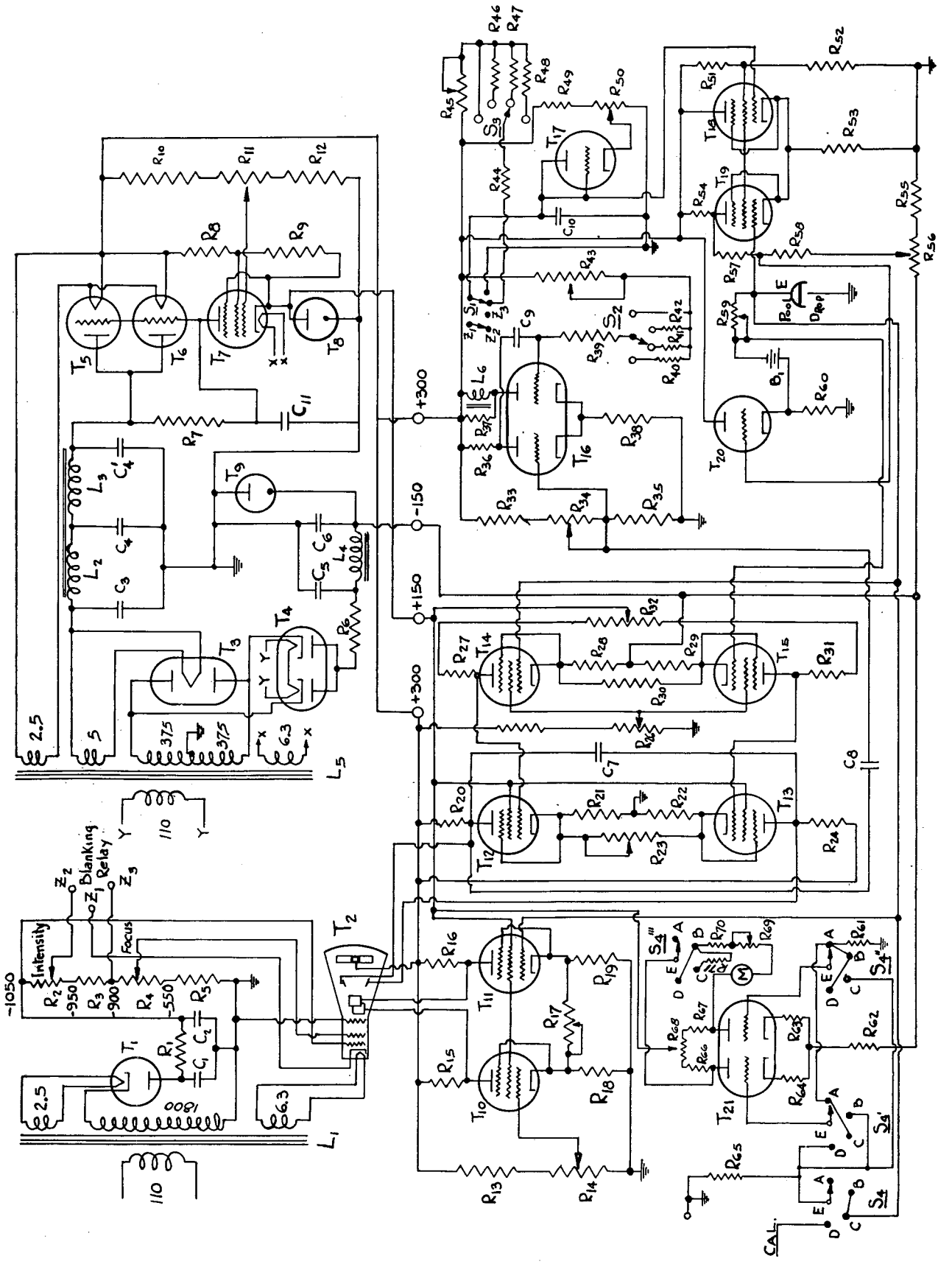
Intensity
Focus
Z Blanking Relay
-1050
-950
-900
-550
1800
110
2.5
5
375
6.3
+300
-150
+150
CAL.

Figure 13. Circuit Diagram of Complete Instrument

B_1.	9-volt C battery	R_{10}, R_{20}, R_{24}, R_{54}.	100 K	R_{34}.	1 megohm	R_{66}.	5 megohms
C_1, C_2.	0.1 μfd., 4000 w.v.d.c.	R_{11}.	40 K, 4-watt pot. (screw driver adjust)	R_{36}.	20 K	R_{68}, R_{67}.	10 K
C_3, C_4, C_5, C_6.	8 μfd., 600 w.v.d.c.	R_{12}.	100 K	R_{39}.	2.2 megohms	R_{68}.	2 K, 4-watt pot. (zero adjustment)
C_7.	1 μfd., 600 w.v.d.c.	R_{13}.	1.5 megohms	R_{40}, R_{42}.	30 megohms	R_{69}.	20 K, 4-watt pot. (calibrated, screw driver adjust)
C_8.	0.05 μfd., 600 w.v.d.c.	R_{14}.	10 K, 4-watt pot. (horizontal position)	R_{41}, R_{46}, R_{47}.	20 megohms	R_{70}.	15 K
C_9, C_{10}.	0.005 μfd., 600 w.v.d.c.	R_{15}, R_{16}.	220 K	R_{43}, R_{44}.	10 megohms, 1-watt pot. (delay, fine adjustment)	R_{71}.	2 K
C_{11}.	1 μfd., 450 w.v.d.c.	R_{17}.	1000, 4-watt pot. (horizontal gain)	R_{48}.	10 megohms, 1-watt pot. (sweep, fine adjustment)	S_1.	D.p.d.t. relay contacts
E_1.	0.05 μfd., 600 w.v.d.c.	R_{18}, R_{19}, R_{21}, R_{22}, R_{37}, R_{38}.		R_{49}.	270 K	S_2, etc.	4-gang selector switch
L_1.	Analyzing cell		10 K	R_{50}.	40 K, 4-watt pot. (sweep max. adjustment)	T_1.	2 X 2
L_2, L_3.	1800-volt secondary, transformer		1000, 4-watt pot. (vertical gain)	R_{51}.	60 K	T_2.	5 LP 7 (DuMont)
L_4.	8 henries, 120 ma.	R_{23}.	67 K	R_{52}.	47 K	T_3.	5 Y 3
L_5.	25 henries, 40 ma.	R_{25}.	40 K, 4-watt pot. (screw driver adjust)	R_{53}.	470 K	T_4.	117 Z 6
L_6.	375-0-375-volt secondary, transformer	R_{26}.	330 K	R_{55}.	33 K	T_5, T_8.	2 A 3
R_1.	11,500 plate relay coil	R_{27}, R_{31}.	270 K	R_{56}.	50 K, 4-watt pot. (sweep min. adjustment)	T_7, T_9.	6 SJ 7
R_2.	500 K, 4-watt pot. (intensity)	R_{28}, R_{29}.	22 K	R_{57}, R_{61}.	5 megohm	T_{10}, T_{11}, T_{12}, T_{13}, T_{14}, T_{15}.	6 SJ 7
R_3.	150 K, 1 watt	R_{30}.	15 K, 4-watt pot. (vertical position)	R_{58}.	2.2 megohms	T_{16}.	6 SN 7
R_4.	250 K, 4-watt pot. (focus)	R_{32}.	1.2 megohms	R_{59}.	10 K, helipot, 0.05% linear	T_{17}.	6 J 5
R_5, R_7.	600 K, 1 watt	R_{33}.	1 megohm, 1-watt pot. (multi-vibrator sensitivity)	R_{60}.	1 K	T_{18}, T_{19}.	6 SJ 7
R_6.	12,500, 20 watts	R_{34}.		R_{62}.	20 K	T_{20}.	6 J 5
R_8.	5000, 10 watts			R_{63}, R_{64}.	4700	T_{21}.	6 SN 7
R_9.	1500, 2 watts						

Unless otherwise noted, all resistors are 0.5-watt.

Figure 14. Cathode-Ray Polarogram of Solution Containing Some Cadmium, Nickel, and Zinc in 1 *N* Ammonium Hydroxide and 1 *N* Ammonium Ion

stage horizontal amplifier. The amplifiers are both supplied with gain controls, and in the case of the vertical amplifier this means that we have two alternative methods of controlling the gain; the other method is through varying the magnitude of the resistor in series with the polarographic cell. Both means of varying the vertical gain of the instrument have their experimental advantages.

The data assembled, sorted, and amplified by this instrument are presented on a cathode-ray tube screen in the form of a voltage-current curve, resulting in a polarogram of normal orientation—i.e., voltage increases negatively from left to right, and current increases upward from the voltage axis. The screen used is of the long-persistence type, having green fluorescence and yellow phosphorescence, the latter persisting in slowly diminishing intensity for 12 to 15 seconds. This enables the operator of the instrument to make accurate estimates of "peak" height, the relative position of the peak along the x-axis, etc. It is also an aid in photographing the curves, if so desired. The cathode-ray tube used is a 5-inch DuMont 5 LP 7.

A vacuum tube voltmeter was built into the circuit for the purpose of setting in, and occasionally checking, the sweep minimum and maximum values. Calibrating jacks are located on the panel for the insertion of a standard cell whenever it is desirable to restandardize the meter.

Figure 15. Curve of Figure 15 Electrically Integrated before Presentation

A complete diagram of the instrument is presented in Figure 13. With the aid of the preceding discussion of the various circuit units, one should be able to chart the entire action of the circuit, from the fall of a drop and the initiation of the time delay, on through to the presentation of the final polarographic curve on the cathode-ray screen.

EXPERIMENTAL RESULTS

The extensive theory of the current-voltage curve has been reviewed by Kolthoff and Lingane (*5*) and Randles (*9*) from both of which sources a thorough understanding of the theory may be received.

Figure 14 is a photograph of the cathode-ray polarogram of a solution containing cadmium, nickel, and zinc ions in a supporting electrolyte of 1 *N* ammonium hydroxide plus 1 *N* ammonium ion. It is immediately apparent that the ordinary polaro-

graphic "steps" have been replaced by peaks, but except for that, the picture is entirely normal. It has been suggested (*9*) that these peaks are a result of ion exhaustion at the electrode surface, this ion exhaustion being clearly visible for a one-drop polarogram, but averaging out in the case of an ordinary polarogram, where hundreds of drops are employed. As shown in Figure 15, these peaks may be transformed into the more conventionally appearing steps by means of electrical integration. This may be more pleasing to the eyes of those engaged in ordinary polarographic work, but because it is a rather artificial technique from which little if anything is gained, the authors have not used it extensively in their work to date.

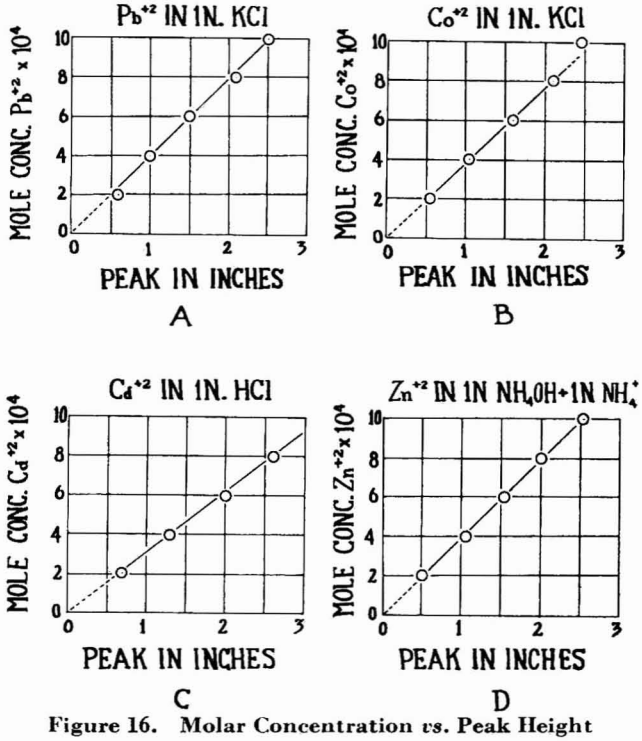

Figure 16. Molar Concentration vs. Peak Height

A. Pb^{++} in 1 *N* KCl *C.* Cd^{++} in 1 *N* HCl
B. Co^{++} in 1 *N* KCl *D.* Zn^{++} in 1 *N* $NH_4OH + NH_4^+$

In the polarogram shown in Figure 14, the sweep voltage was not started at zero potential, but at −0.30, so that an unwanted oxygen peak could be omitted from the photograph. Dry nitrogen was not available at the time of photographing, and although the second oxygen peak was eliminated with the ordinary nitrogen on hand, the first peak, occurring in the early portion of the curve, was still fairly large. Thus, the true origin of the curve shown was located 0.56 inch to the left of the apparent origin as seen in the photograph. This, of course, refers to the original scale on the cathode-ray screen. The displacement of the three ion peaks from this true origin are in direct proportion to the half-wave potentials as obtained from an ordinary polarograph. The small peak at the far left of the photograph is either part of the tail end of the oxygen break, or a trace of impurity in the solution, perhaps a small amount of cobalt.

Many curves similar to the one just discussed were obtained. Several supporting electrolytes have been employed, including 1 *N* ammonium hydroxide plus 1 *N* ammonium ion, 1 *N* potassium chloride, 1 *N* hydrochloric acid, 1 *N* and 2 *N* potassium hydroxide, and 1 *N* sodium hydroxide. In all cases the cathode-ray polarograph gave half-wave potentials within ±1.5% of the values obtained in the usual manner, and in the majority of cases the results were within ±1.0%. More than fifteen of the common metal ions were tested in one or more of the supporting electrolytes, and it was found that the instrument could discriminate between two ions if their half-wave potentials were separated by at least 0.1 volt. If the half-wave potentials were separated by less than 0.1 volt, the two peaks merged and were indistinguishable from one another. This is naturally not a sharp dividing line, but it provides a suitable rule of thumb.

The usefulness of the cathode-ray polarograph as a quantitative analytical instrument is best demonstrated by the curves of Figures 16 and 17. In Figure 16 the molar concentration for four representative ions, lead, cobalt, cadmium, and zinc, are plotted against the peak height of the breaks observed at the indicated concentrations. The results show that the instrument responds linearly with respect to concentration, up to concentrations of 10^{-3}, in general. One serious drawback of this method in quantitative work is the difficulty encountered in accurately measuring the peak height. It can be done accurately, but it is very painstaking and tedious, and this method should be used only when no other will suffice. A second method, suggested by Randles (*9*), involves adjusting the value of the resistance in series with the polarographic cell until the peak is exactly equal to some preselected standard height. This adjustment is a much easier task, from an operational standpoint, than the measurement of some random peak height, and it has the additional advantage of always operating the amplifiers at the same bias level, thereby eliminating the effects of any possible nonlinearity of amplifier response. This method of determining concentrations can be represented mathematically as follows:

$$RK = \alpha \qquad (5)$$

where R is the vertical amplifier input resistance (the resistor in series with the cell), K is the ion concentration, and α is a constant, represented here by the fixed, standard peak height. It is seen that this expression is a hyperbola asymptotic to the two axes.

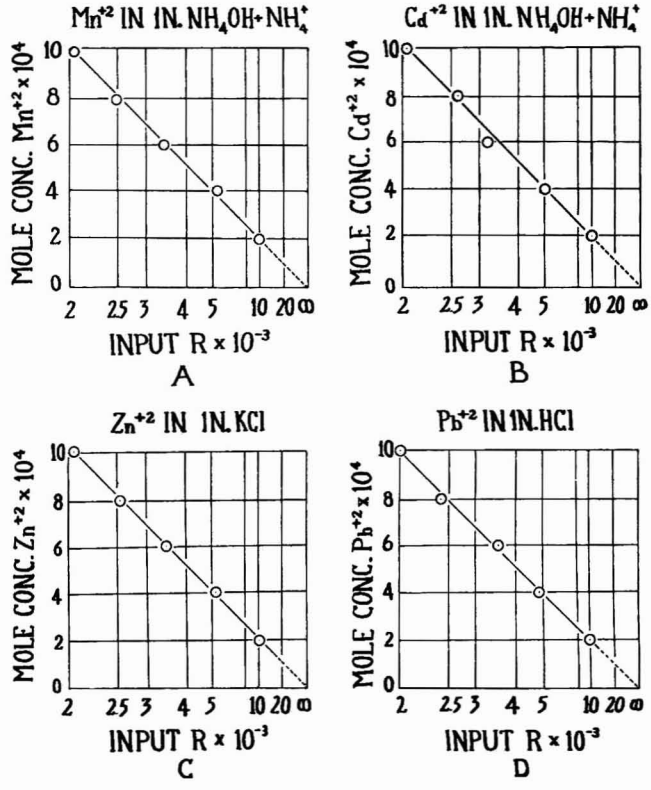

Figure 17. Amplifier Input Resistance vs. Molar Concentration

A. Mn^{++} in 1 *N* $NH_4OH + NH_4^+$ *C.* Zn^{++} in 1 *N* KCl
B. Cd^{++} in 1 *N* $NH_4OH + NH_4^+$ *D.* Pb^{++} in 1 *N* HC

If then, R and K are plotted against one another on either log-log or hyperbolically ruled (reciprocally ruled) paper, the resultant curve should be linear. Figure 17 shows the results of several experiments made with various ions and supporting electrolytes, plotted on hyperbolically ruled paper.

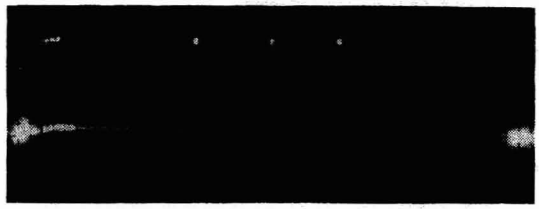

Figure 18. Curve of Figure 15 Electrically Differentiated Before Presentation

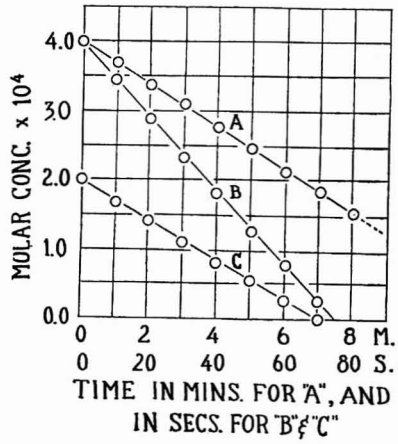

Figure 19. Zero-Order Reaction Plots Obtained by Ultraviolet Radiation Decomposition

A. *p*-Toluidine diazo in pH 3.0
B. Ethyl benzyl diazo, double tin salt, in pH 4.2
C. Diethyl amino diazo, double zinc salt, in pH 4.2

It was found that the precision obtainable with the cathode-ray polarograph in quantitative analysis was ±4% when the first of the above two techniques was used, and within ±2% when the second was used. In general, the precision improved up to concentrations of 2 or 3 × 10^{-4}, with little or no improvement noted for concentrations above this value. For very small concentrations the finite width of the cathode-ray trace was a definite limiting factor. Just as in ordinary polarography, the principal limiting factor in the ability of the instrument to separate the constituent ions into well-defined, easily measurable breaks is the relative concentrations of the various ions in solution. If the half-wave potentials of two ions are separated by (1) at least 0.5 volt, the cathode-ray polarograph performs satisfactorily for no more than a tenfold difference in concentration; (2) at least 0.25 volt, performance is satisfactory for no more than a five fold difference in concentration; and (3) at least 0.1 volt, performance is satisfactory only if the concentration difference is less than twofold. Again, these values are not meant to constitute a hard and fast rule, but are given as a convenient rule of thumb.

In most of the authors' experimental work to date, the amplifier controls were set so that 2 inches along the x-axis corresponded to 1 volt, and 1 inch along the y-axis corresponded to a diffusion current of 1 μa. Although these controls can be set with great accuracy, two methods of standardizing the results were still employed. In one method a known amount of an ion that is not present in the sample is added; the height of the peak resulting from this "pilot" ion is used to calibrate the current axis. In the second method, a known amount of the ion being analyzed is added to the cell, and the difference in peak height before and after the addition of this known amount is used to calibrate the current axis. In cases where best possible precision is desired, both standardizing methods are employed.

For purely qualitative results, much more positive separation of the ion breaks may be had if the output of the amplifiers is differentiated prior to the cathode-ray presentation. This results in the transformation of the peaks into sharply defined spikes, as shown in Figure 18, which is the differentiated form of the curve of Figure 14. One difference in the operating conditions of the polarograph at the times when these two photographs were taken is that for Figure 19 the sweep was started at zero potential, instead of at −0.30 volt as for Figure 14. Thus, Figure 18 shows more clearly the proportionality which exists between the half-wave potentials represented by the breaks in the curve, and the displacement of these breaks from the origin of the curve. Unfortunately, in order to get satisfactory differentiation it was necessary to use a differentiator which clipped off the tops of the spikes; this at once invalidated any possible application of these differentiated curves to quantitative determinations.

As interesting as these above results are, it is the feeling of the authors of this paper that the contributions of the cathode-ray polarograph to inorganic polarography will be secondary to those that will be made in the organic and reaction kinetics fields. Some preliminary work in these fields indicates the potentialities of the instrument. To date the authors have been more interested in the application of the cathode-ray polarograph to the study of reaction rates and kinetics than to pure organic analysis, but excellent results have been obtained in the analysis of formaldehyde in slightly basic solutions in the presence of acetone, and in the analysis of some azo dyes. (This analysis had to be performed quickly, because formaldehyde and acetone react to form γ-ketobutanol in basic media.) It is also felt that the application of the instrument to the field of organic analysis is strongly implied in the following presentation of some reaction rate curves for a few organic reactions.

The cathode-ray polarograph can be used to observe and measure the rate of reactions whenever any of the reactants or

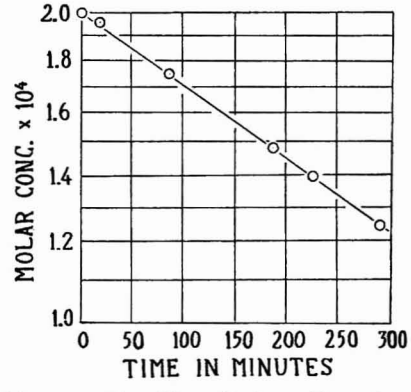

Figure 20. First-Order Reaction Plot Obtained by Heat Decomposition

Double zinc salt of diethyl amino diazo at 50° C., pH 4.2

reaction products gives a polarographic break. In addition, many times it is possible to see the formation and subsequent disappearance of some intermediate compound. Types of reactions that the instrument here described has been used to observe are: (1) relatively rapid light-sensitive reactions, (2) heat decomposition of diazos and diazo salts, (3) formation of azo dyes by diazo-

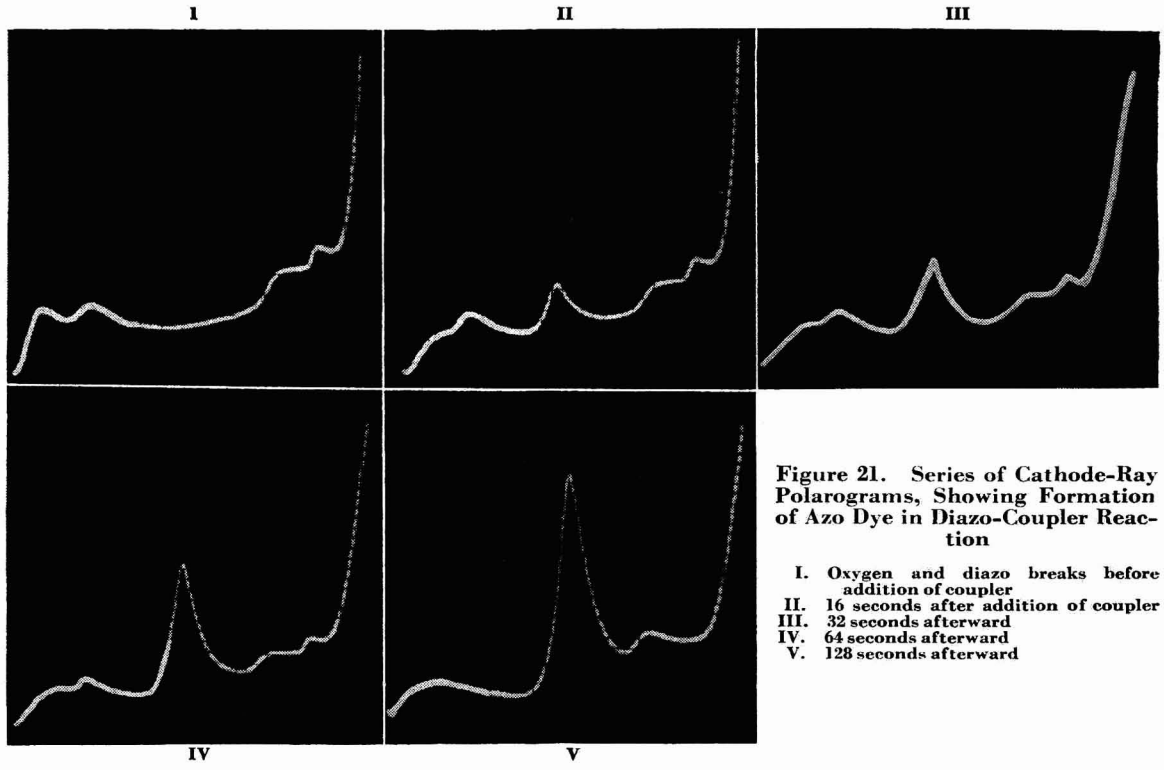

Figure 21. Series of Cathode-Ray Polarograms, Showing Formation of Azo Dye in Diazo-Coupler Reaction

I. Oxygen and diazo breaks before addition of coupler
II. 16 seconds after addition of coupler
III. 32 seconds afterward
IV. 64 seconds afterward
V. 128 seconds afterward

coupler reactions, and (4) reaction between formaldehyde and acetone in slightly basic media, with the formation of γ-keto-butanol.

Three examples of the first type of reaction mentioned above are shown in Figure 19, which represents the curves obtained when the diazo and diazo salts indicated were exposed to ultraviolet radiation from an H-6 lamp placed 6 inches (15 cm.) from the polarographic cell. As can be seen from the linear concentration-time plot, these three examples are excellent illustrations of zero-order reactions. Apparently the rate-controlling factor is the absorption of a photon of light; hence the reaction rate is independent of concentration. These reactions all took place at a temperature of 4° C., precluding the possibility of simultaneous heat decomposition of the reactants.

Figure 20 illustrates a first-order reaction, the heat decomposition of a diazo salt at 50° C. This is a relatively slow reaction at this temperature, but it is included to show that the stability of the instrument is more than sufficient to allow for the plotting of reactions which take, not seconds or minutes, but hours to complete. In addition to this, the curve shown is a good example of a first-order reaction, and may, of itself, be of some interest.

Figure 21 presents a series of photographs showing the formation of an azo dye from the coupling of sulfanilic acid diazo and sulfonated pyrazalone. The first photograph shows a curve with four breaks. The first and third of these are caused by unswept, residual oxygen, while the second and fourth show the presence of sulfanilic acid diazo. The second frame shows the curve resulting 16 seconds after the addition of the coupler; the third, fourth, and fifth frames show the curve after 32, 64, and 128 seconds, respectively. In this last frame the reaction has been completed. The initial concentrations in the cell were 10^{-4} molar for the diazo, and 2×10^{-4} molar for the coupler. Table III gives the concentrations for the two reactants and the reaction product, as measured from the photographs, at the indicated times after the addition of the coupler to the cell.

By substituting the above values in the formula for k for a second order reaction:

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)} \qquad (6)$$

where a and b are the initial concentrations of the coupler and diazo, respectively, and the other quantities are as indicated in Table III; the values for k are calculated as follows:

At 16 sec. k = 80.7 liters moles^{-1} sec.$^{-1}$
At 32 sec. k = 79.4 liters moles^{-1} sec.$^{-1}$
At 64 sec. k = 82.9 liters moles^{-1} sec.$^{-1}$

resulting in an average value for k of 81.0 liters moles^{-1} sec.$^{-1}$, indicating clearly that this reaction is of the second order. Multiplying the above value for k by 60 gives the value for k in the more conventional units, 4860 liters moles^{-1} min.$^{-1}$. This value agrees well with the results observed by Elofson, Edsberg, and Mecherly (*3*), who have investigated many of the slower diazo-coupler reactions by ordinary polarographic technique.

CONCLUSION

An improved cathode-ray polarograph has been designed around readily available components. This instrument can be used as a qualitative and quantitative analytical tool, for both inorganic systems and many organic systems, and it is capable of following rapid, as well as slow, reactions of zero, first, and

Table III. Data Obtained by Coupling Sulfanilic Acid Diazo with Sulfonated Pyrazolone

Time after Addition of Coupler, sec.	Molar Concn. of Azo Dye Formed, x	Molar Concn. of Diazo Remaining, $b - x$	Molar Concn. of Coupler Remaining, $a - x$
0	0.00	1.00×10^{-4}	2.00×10^{-4}
16	0.22×10^{-4}	0.78×10^{-4}	1.78×10^{-4}
32	0.37×10^{-4}	0.63×10^{-4}	1.63×10^{-4}
64	0.58×10^{-4}	0.63×10^{-4}	1.42×10^{-4}
128	1.00×10^{-4}	0.00	1.00×10^{-4}

second order. There is also no reason to doubt that the instrument is capable of following third-order reactions as well. It is felt that the real contributions to be made by this instrument lie in this latter field, particularly in following fast reactions of the types which are completed in the range of 30 to 150 seconds.

ACKNOWLEDGMENT

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Application of the Distribution Law to Analytical Polarography

Analysis of Compounds Having Similar Half-Wave Potentials and Chemical Properties

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A method of polarographic analysis of compounds having the same or closely similar half-wave potentials is proposed. It is an adaptation of the method of Osburn and Werkman, which is based on differences of distribution of these materials between two immiscible solvents. The method, although applied here to polarographic analysis, can be used where any measurement, physical or chemical, is made to determine the aggregate sum of the individual components in one of the solvents. The tentative name "partition polarography" is proposed for this particular application. Formulas have been deduced which predict the probable accuracy of such a method and permit selection of optimum experimental conditions for each system with a minimum of experimental work. The method has been applied to the analysis of mixtures of acetaldehyde, propionaldehyde, and *n*-butyraldehyde.

SINCE the inception of polarographic analysis in 1922 by Heyrovský and his co-workers (*5*) of Charles University, the pace of fundamental and applied research has rapidly gained momentum. Today the polarograph has a secure position in the analytical, physical, and organic laboratories as a most powerful tool. There are, however, certain inherent limitations in polarography, some of which are due to electrode properties, others to the properties of the materials subjected to electrolysis. It is with the latter that this report is concerned.

It has been known for some time that many ions and compounds cannot be differentiated polarographically, owing to the juxtaposition of their half-wave potentials. The problem is not serious in inorganic analyses because most ions in this class differ markedly in their chemical properties. Thus, separation can be achieved by precipitation, complex formation, or neutralization. Examples of such techniques may readily be found in the literature (*8*). A notable exception is, of course, the alkali metals. In organic polarography the situation is not so fortunate. The functional group or groups which determine the reducibility of the compound usually play a predominant part in its chemical behavior. Thus, saturated aliphatic aldehydes, with the exception of formaldehyde, all reduce at about −1.80 volts *vs.* the saturated calomel electrode, peroxides at about −1.50 volts *vs.* the saturated calomel electrode, etc. Because of this phenomenon, polarographic analysis of organic compounds has thus far necessarily concerned itself with types of compounds rather than single compounds. The analyses, therefore, are for total peroxides, total aldehydes, total naphthalenes, etc. Frequently, this supplies all the data required, but occasionally the need is for data concerning the individual compounds. It is obvious that chemical differentiation of single compounds is not feasible in the above-mentioned cases and that resort to differences in physical properties might offer some promise in attacking the problem.

One of the earliest uses of partition constants in polarography was made in 1935 by Gosman (*4*). In order to determine the acetaldehyde content of ether, he extracted the ether twice with aqueous lithium hydroxide. The ratio of the two waves gave him the partition constant and he then calculated the original concentration of acetaldehyde. Gnyubkin *et al.* (*3*) studied the reduction of the wave heights of volatile aldehydes when deoxygenating the polarographic solution with hydrogen. Gnyubkin noted that the rate of loss of acetaldehyde, propionaldehyde, and *n*-butyraldehyde differed markedly. Using Raoult's law, he derived an expression for calculating the loss of each aldehyde with time, and by making wave-height measurements after scrubbing with a known quantity of hydrogen, he could then solve two simultaneous equations with two unknowns. This method is applicable only to volatile constituents, but has the advantage that devious means need not be adopted to avoid the necessity of deoxygenating the solution with scrubbing. Knudsen and Grove (*7*) developed an expression for determining the optimum conditions of extraction for quantitatively separating two materials closely related physically and chemically. Their work appeared too time-consuming for adaptation to an analytical technique.

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Recently, Tsai and Fu (*15*) published a critical analysis of the use of partition constants in the methods of Behrens (*1*) and Osburn and Werkman (*10*). This method was developed for the determination of fatty acids of low molecular weight (excepting formic) when present in mixtures. It was based on the fact that each fatty acid has a different extraction coefficient, which is the fraction of the total remaining in solvent w when extracted by solvent s. A thorough discussion was presented on the effects of multiple extractions on accuracy in the method and means of avoiding gross errors in analysis due to insufficient difference in the extraction coefficients and of variation of these coefficients with concentration due to association and dissociation of the acids. This paper is concerned with the application of the technique of Osburn and Werkman (*10*) to polarographic analysis.

THEORETICAL

In much of the previous analytical polarography using selective extraction as a separation tool, emphasis has been laid on processes that quantitatively isolate the desired component. It would appear, however, that if only some selectivity is achieved, one could mathematically deduce the original concentrations involved. We know that if a solute A is in equilibrium between solvents w and s, the ratio of the concentration of A in s (C_{As}) to that in w (C_{aw}) is given by the distribution coefficient, k_A.

$$\frac{C_{As}}{C_{Aw}} = k_A \tag{1}$$

For purposes of the discussion which follows it is convenient to evaluate the fraction α_A (the extraction coefficient of Tsai and Fu), of component A which remains in a volume, V_w, of solvent w after extraction with a volume V_s, of solvent s. If C°_{Aw} is the original concentration of A in w, it follows that:

$$\alpha_A = \frac{C_{Aw}}{C^{\circ}_{Aw}} = \frac{1}{1 + k_A\frac{V_s}{V_w}} \tag{2}$$

For Equation 2 to be valid, it is necessary that there be no appreciable change in volume of either phase during the extraction. This condition would require that C_{Aw} be small and that each of the two solvents initially be saturated with the other or that the mutual solubilities be very low. The condition of very dilute solutions is also necessary if the solutions are to obey the simple distribution law. It follows that, for best results, the solutions under examination must be as dilute as possible without a major loss in analytical precision. Fortunately, polarographic analysis is at its optimum in dilute solutions (ca. 10^{-4} to 10^{-5} M). Equation 2 is useful because it permits calculation of α_A at other ratios of V_s/V_w when it is known at one ratio.

One can develop an expression for determining the concentrations of a series of components having the same $E_{1/2}$ values but different distribution properties by means of polarography.

The Ilkovič equation can be simplified to

$$i_d = KC \tag{3}$$

where the symbols have their usual significance. In a mixture of two solutes in water, the polarographic total wave height is the sum of the individual wave heights, providing that exaltation, suppression, and chemical reaction do not take place. Thus,

$$K_AC_A + K_BC_B = i_0 \tag{4}$$

where K_A is the slope of the calibration curve for solute A, C_A is the concentration of solute A, K_B and C_B are corresponding values for solute B, and i_0 is the measured diffusion current of the unextracted mixture in water. If now a volume, V_w, of the water solution is extracted n times with equal volumes, V_s, of an immiscible solvent under carefully controlled conditions so that equilibrium is reached in each extraction, each of the solutes will behave as if the other were not present, and a fixed fraction of each α_A^n and α_B^n (see Equation 2) will be left in the water layer. The diffusion current of the extracted aqueous layer is designated as i_n and it is apparent that i_n is determined by the following relationship:

$$\alpha_A^nK_AC_A + \alpha_B^nK_BC_B = i_n \tag{5}$$

We now have two simultaneous equations with two unknowns —i.e., Equations 4 and 5—in which α and K are previously determined values, i_n is measured, and C for each component is therefore the unknown. For a mixture of R solutes, the general form of the equation is:

$$\begin{aligned} &K_AC_A + K_BC_B + \ldots\ldots\ldots\ldots K_RC_R = i_0 \\ &\alpha_A^nK_AC_A + \alpha_B^nK_BC_B + \ldots\ldots\ldots\ldots \alpha_R^nK_RC_R = i_n \\ &\alpha_A^iK_AC_A + \alpha_B^iK_BC_B + \ldots\ldots\ldots\ldots \alpha_R^iK_RC_R = i_j \\ &\alpha_A^zK_AC_A + \alpha_B^zK_BC_B + \ldots\ldots\ldots\ldots \alpha_R^zK_RC_R = i_z \end{aligned} \tag{6}$$

It will be shown later that for any particular analysis of this type there exist optimum values for the number of extractions, as well as for the ratio of the volumes of the two solvents used in each extraction.

From an examination of Equations 6 one can deduce several requirements placed upon this type of analysis. The first is strict additivity of diffusion current, the second is constancy of the partition constants in the working concentration range, the third is the good separation of α values, and the fourth is the need for accuracy of the highest order in all polarographic measurements to reduce magnification of errors that accompanies the use of series of simultaneous equations. The first two conditions can be verified experimentally. The third is obvious from a consideration of the two extremes of differences in α. If, in a two-component mixture, $\alpha_A = 1.00$ and $\alpha_B = 0$, the diffusion current after the first extraction is due solely to solute A and, in effect, this becomes a simple separation technique with no need for simultaneous equations. At the other extreme of $\alpha_A = \alpha_B$ both solutes will be extracted to exactly the same extent. Because no selectivity will result, the method will break down. A more detailed examination of the propagation of experimental errors in this analytical scheme follows.

Propagation of Experimental Errors in Partition Polarography. For the sake of simplicity we shall first examine the case of analysis of mixtures of only two solutes, A and B, which satisfy the conditions discussed above. By simultaneous solution of Equations 4 and 5, we obtain:

$$C_A = \frac{i_0\alpha_B^n - i_n}{K_A(\alpha_B^n - \alpha_A^n)} \tag{7}$$

$$C_B = \frac{i_0\alpha_A^n - i_n}{K_B(\alpha_A^n - \alpha_B^n)} \tag{8}$$

It has been shown (*12*) that if an indirectly measured quantity, Q, is related to several independent directly measured quantities —$q_1, q_2, \ldots q_n$—by the equation

$$Q = f(q_1, q_2, \ldots q_n) \tag{9}$$

and we know the probable errors $\Delta q_1, \Delta q_2 \ldots \Delta q_n$ in $q_1, q_1 \ldots q_n$, then the probable error in Q, ΔQ, is given approximately by the equation

$$\Delta Q = \pm\left[\left(\frac{\partial f}{\partial q_1}\right)^2(\Delta Q_1)^2 + \left(\frac{\partial f}{\partial q_2}\right)^2(\Delta Q_2)^2 + \ldots\left(\frac{\partial f}{\partial q_n}\right)^2(\Delta Q_n)^2\right]^{1/2} \tag{10}$$

We may combine Equation 10 with 7 and 8 to predict the probable over-all accuracy of the proposed scheme of analysis. It is necessary in this computation to consider the following experimentally measured variables: i_0, i_n, K_A, K_B, α_A, and α_B. Thus we obtain ΔC_A and ΔC_B, the probable errors in C_A and C_B, respectively.

Table I. Calibration Data for System Acetaldehyde-Propionaldehyde

Component	V_s/V_w	Extraction Coefficient, α	$\Delta\alpha$	Partition Coefficient, k (Caled.)	Δk	Ilkovič Constant, K, μa./Mg./50 Ml.	ΔK
Acetaldehyde	1	0.741	0.004	0.350	0.007	2.80	0.01
Propionaldehyde	1	0.323	0.002	2.096	0.019	2.07	0.01

Table II. Variation of Extraction Coefficients with Ratio of Benzene to Water

V_s/V_w	α_A	$\Delta\alpha_A$	α_B	$\Delta\alpha_B$
5	0.364	0.005	0.0871	0.007
2	0.588	0.005	0.1926	0.0014
1	0.741[a]	0.004[a]	0.323[a]	0.002[a]
0.5	0.851	0.0025	0.488	0.002
0.2	0.935	0.0012	0.705	0.0019

[a] Measured values.

$$\Delta C_A = \pm \frac{1}{K_A(\alpha_B^n - \alpha_A^n)} [\alpha_B^{2n}(\Delta i_0)^2 + (\Delta i_n)^2 + n^2\alpha_B^{2n-2} K_A^2 C_B^2 (\Delta\alpha_B)^2 + n^2\alpha_A^{2n-2} C_A^2 K_A^2 (\Delta\alpha_A)^2 + C_A^2(\alpha_B^n - \alpha_A^n)^2 (\Delta K_A)^2]^{1/2} \quad (11)$$

$$\Delta C_B = \pm \frac{1}{K_B(\alpha_A^n - \alpha_B^n)} [\alpha_A^{2n}(\Delta i_0)^2 + (\Delta i_n)^2 + n^2\alpha_A^{2n-2} K_B^2 C_A^2 (\Delta\alpha_A)^2 + n^2\alpha_B^{2n-2} C_B^2 K_B^2 (\Delta\alpha_B)^2 + C_B^2(\alpha_A^n - \alpha_B^n)^2 (\Delta K_B)^2]^{1/2} \quad (12)$$

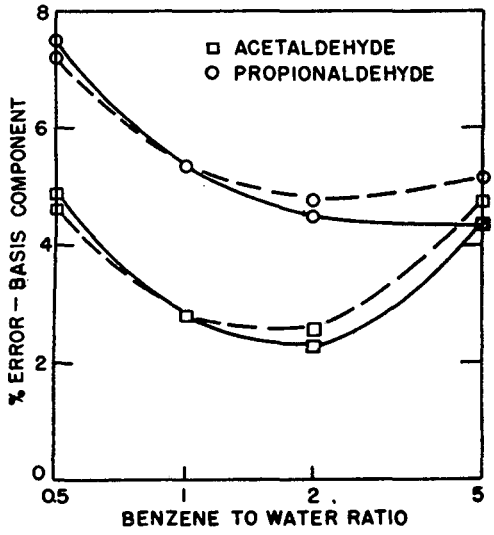

Figure 1. Effect of Variation of Ratio of Benzene to Water on Accuracy of Analysis

$C_A = C_B$, $n = 1$
——— α_A determined for each value of V_s/V_w
- - - - α_A determined for $V_s/V_w = 1$

From Equations 2, 11, and 12, we can deduce much useful information relative to the selection of optimum conditions for carrying out a given analysis, the accuracy with which we can expect under a given set of conditions and the effect of uncertainties in each of the experimentally measured quantities on the over-all accuracy.

For the purpose of illustration, let us consider the analysis of mixtures of acetaldehyde, A, and propionaldehyde, B, originally present in aqueous solution with benzene as the extraction solvent. Calibration data for this system taken from the experimental part of this paper are shown in Table I.

We shall assume that $\Delta i_0 = 0.01 i_0$ and $\Delta i_n = 0.01 i_n$ and calculate the resulting errors in concentrations for a number of hypothetical conditions. This assumption of constant percentage accuracy in the measurement of diffusion coefficients is essential to the attainment of highest accuracy in this scheme of analysis. In general, it will mean that either the aliquot taken for analysis from the extracted solution must be somewhat larger than that taken from the original solution or that a greater current sensitivity must be used in measuring the polarographic wave obtained from the extracted solution. If larger aliquots are taken it is necessary to correct the diffusion currents obtained accordingly before applying Equation 7 and 8. If neither of these precautions is taken Δi_n must be taken as $0.01 i_0$ and larger errors will be found, especially in the case of the components of low α values.

Effect of Ratio of Solvent to Water, V_s/V_w. It will be noted in Table I that α_A and α_B for $V_s/V_w = 1$ were the directly measured variables. The uncertainties in their values, $\Delta\alpha_A$ and $\Delta\alpha_B$, respectively, were estimated from the precision of the calibration data. The partition coefficients k_A and k_B, were obtained by computation from Equation 2 and their uncertainties by combining Equations 10 and 2. Thus

$$\Delta k_A = \pm \frac{\Delta\alpha_A V_w}{\alpha_A^2 V_s} \quad (13)$$

Equation 13 may then be used to compute $\Delta\alpha_A$ and $\Delta\alpha_B$ for other values of V_s/V_w. Table II lists computed values for α_A, $\Delta\alpha_A$, α_B, and $\Delta\alpha_B$ for a few values of V_s/V_w.

We may now use Equations 11 and 12 to compute the effect of variation of V_s/V_w on the over-all accuracy of the analysis. This has been done for the case of equal concentrations of A and B, and $n = 1$, with the results shown in Table III and graphically in Figure 1. The errors have been calculated for two cases: (1) The α values used in the analysis are computed from those corresponding to $V_s/V_w = 1$, and (2) they are determined directly. In the latter case $\Delta\alpha$ is assumed to be 0.006α, which is in agreement with the precision of the experimental work. It is interesting to note that the optimum value of V_s/V_w is different for the two components, being greater than 5 for propionaldehyde and about 2 for acetaldehyde. A value of 2 seems to be about optimum. However, this might not be the case for other values of C_A and C_B.

Table III. Effect on Over-all Accuracy of Variation of V_s/V_w

($C_A = C_B$, $n = 1$)

	Computed Error, % of Amount Present			
	ΔC_A		ΔC_B	
V_s/V_w	α_A determined	α_A computed	α_B determined	α_B computed
5	4.2	4.7	4.3	5.2
2	2.3	2.5	4.5	4.7
1	2.7	...	5.4	...
0.5	4.8	4.6	7.5	7.3

The improvement in accuracy when going from $V_s/V_w = 1$ to $V_s/V_w = 2$ is small and would, therefore, be difficult to verify experimentally. Because the computations were performed at a later date than the experimental work, it is fortunate indeed that the experimental conditions chosen after only a cursory examination of relative α values should be so close to the optimum.

Table IV. Effect on Accuracy of Varying Number of Extractions

($C_A = C_B$, $V_s/V_w = 2$)

	% of Amount Present	
n	ΔC_A	ΔC_B
1	2.3	4.5
2	1.9	3.5
3	2.2	3.9
4	2.6	4.3

EFFECT OF NUMBER OF EXTRACTIONS. The effect of the number of extractions, n, has been computed for the case $C_A = C_B$, $V_s/V_w = 2$, with the results presented in Table IV. It will be noted that two extractions lead to best accuracy for each component, although the gain in precision is rather small in going from $n = 1$ to $n = 2$.

EFFECT OF VARIATION IN RELATIVE CONCENTRATIONS, C_A/C_B. The expected errors in analyzing other mixtures of acetaldehyde and propionaldehyde under these conditions are given in Table V and Figure 2.

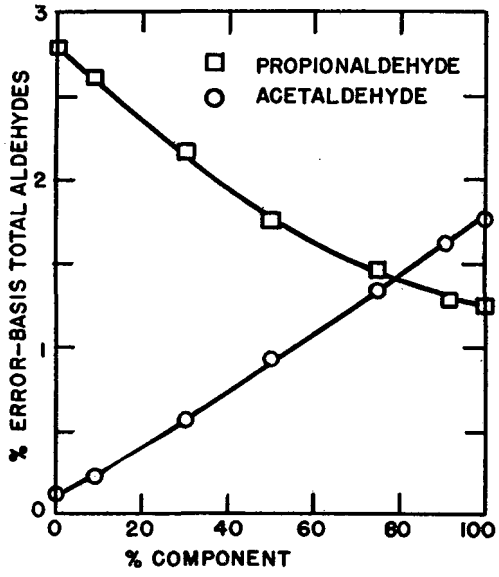

Figure 2. Variation of Accuracy of Analysis with Composition

$n = 2$
$V_s/V_w = 2$

The accuracy for each component is best when propionaldehyde is the major component, but for every condition studied the accuracy for acetaldehyde (expressed as per cent of total aldehydes) is better than that for propionaldehyde. This is largely in consequence of its larger K and α values, as may be seen from inspection of Equations 11 and 12. In general, the accuracy of the method proposed here is best for the component which gives the largest diffusion current for unit weight and is extracted to the lesser extent. Furthermore, $\alpha_A^n - \alpha_B^n$ should be as large as possible.

Table V. Effect of Varying Relative Concentrations of Components

($V_s/V_w = 2$, $n = 2$)

	ΔC_A		ΔC_B	
C_A/C_B	% of amount present	% of total aldehyde	% of amount present	% of total aldehydes
∞	1.77	1.77	∞	2.8
10	1.78	1.62	28.5	2.6
3	1.79	1.34	9.1	2.2
1	1.86	0.93	3.5	1.75
0.3	2.46	0.57	1.91	1.46
0.1	2.50	0.23	1.41	1.29
0	∞	0.12	1.25	1.25

Ternary and Higher Systems. The extension of the method for predicting over-all accuracy to the case of analysis of more complex systems is straightforward. However, the computation becomes very laborious, owing to the large number of possible combinations of different values of V_s/V_w and numbers of extractions which might be employed. Equations analogous to Equations 11 and 12 have been derived for the ternary system acetaldehyde–propionaldehyde–n-butyraldehyde for the case $V_s/V_w = 1$, and measurements of i_0, i_1, and i_2.

For comparison with the results for the binary system, it should suffice to give the results for the case of equal concentrations of the three aldehydes. The following errors are predicted corresponding to a 1% error in diffusion currents: acetaldehyde 4.3%, propionaldehyde 20%, and n-butyraldehyde 29%. Comparison of these figures with the data of Table III indicates a gross reduction of accuracy on the introduction of the third component.

APPARATUS

A Sargent Model XXI recording polarograph was used complete with constant-temperature bath, and H-type thermostated cell with a saturated calomel electrode as the external anode.

An equilibration unit was constructed by mounting a $^1/_3$-hp. motor (1760 r.p.m.) and an $18^2/_3$ reducing head above a 25° ± 0.2° C. open-top constant-temperature bath. A 4-inch (10-cm.) diameter disk fastened to the output shaft of the reducing head provided the drive for an extension shaft extending below the surface of the water. The shaft ended in a Bunsen clamp which traveled through a 4-inch vertical stroke and remained below the surface at all times. The upper end of this shaft extended through a sliding bearing to a knuckle coupling to a second shaft which was fastened to a hole on the outer edge of the disk. The speed was about 180 strokes per minute.

Extraction bottles were prepared by hand lapping the glass stoppers of 30- and 60-ml. small-mouthed ⅋ bottles into the necks until a close fit was obtained.

REAGENTS

All aldehydes were Eastman Kodak white label.
Lithium hydroxide, Mallinckrodt, purified.
Lithium chloride, Mallinckrodt, analytical reagent.
Lithium sulfate, Mallinckrodt, analytical reagent.
Carbon tetrachloride, Baker and Adamson, C.P.
Benzene, Baker and Adamson, C.P.
Gelatin, E. H. Sargent Co., purified pigskin gelatin for polarographic use. Prepared in 0.2% concentration and preserved with a few drops of toluene.

METHOD

The method used in this study is rather simple. If a binary mixture is to be analyzed, dilute an aliquot of the water solution to 50 ml. in a volumetric flask containing 5 ml. of 0.5 M lithium chloride and 1 ml. of 0.2% gelatin. Transfer the solution to the cell and adjust the initial potential to −1.60 volts, the span potential to 2.0 volts, and the sensitivity to yield a satisfactory wave. Adjust the pen position with the down-scale helipot to compensate for the oxygen waves. Record the polarogram from −1.60 to −2.00 volts. Measure the deflection at −1.60 and −1.975 volts and subtract. Calculate the current in microamperes. This is i_0. Pipet another aliquot (usually 10 to 20 ml.) of the aqueous solution into an extraction bottle containing exactly the same amount of benzene if V_s/V_w is to be 1. Stopper tightly and clamp into place with the Bunsen clamp (below the surface of the water). Shake for 5 minutes, allow to settle for 1 minute, and remove the bottle from the bath. Rapidly pipet an aliquot of the water layer into a 50-ml. volumetric flask containing the same amount of lithium chloride and gelatin as before. Dilute to the mark and obtain the polarogram as above. Measure and compute the diffusion current in microamperes. Adjust this value so that the same aliquot for i_0 and i_1 will be considered. For a ternary mixture extract the extracted solution a second time and polarograph to get i_2.

To obtain the α values of each aldehyde, prepare solutions of each aldehyde over a range of concentrations. Treat each solution as described above—i.e., polarograph the original solution and extracted solution and determine the ratio of the diffusion current of the extracted solution to that of the original (on an equal aliquot basis). This ratio is for $V_s/V_w = 1$, the solvent to water ratio used in all the experimental work which follows. Because the experimental part of this paper was terminated before the mathematical considerations were studied, it was not realized that slightly different conditions were advantageous.

PRELIMINARY STUDIES

A series of short studies was made to establish the best conditions for the analyses—i.e., polarographic measurements and extractions.

Temperature Control. By carefully varying the temperature

it was found that a 1.5° C. change in temperature from 25° resulted in a 4.5% shift in partition constant of acetaldehyde.

Time for Equilibrium to Be Reached. In a benzene-water system with the different aldehydes as solutes and varied times of shaking in the unit described, equilibrium was achieved in less than 2 minutes. As an added safety factor 5 minutes were adopted as standard extraction time.

Extraction Bottles. Loss of volatile materials through the stopper was a serious source of trouble until all the glass stoppers were carefully ground in with a fine Carborundum.

Choice of Extraction Solvent. In the initial portion of this study, carbon tetrachloride was used as the extraction solvent because of its immiscibility with water, prompt separation after shaking, and general chemical and polarographic inertness. After the study had progressed to the point where binary systems were being analyzed and where larger aliquots of the aqueous layer were being polarographed to get a measurable wave, a systematic error appeared which vitiated the quantitative nature of most of the data. A study was made therefore of the polarographic effect of water equilibrated with carbon tetrachloride on the aldehyde waves. Surprisingly enough, it appeared that the trace quantities of carbon tetrachloride dissolved or dispersed in the aqueous phase underwent a reduction at the potentials involved. A clear "step" was not obtained, but both the residual and diffusion current slopes increased markedly, the latter more than the former, which resulted in i_l values that were always too high. This effect could be estimated by using larger aliquots of the water layer, each having the same total quantity of acetaldehyde. A survey of the literature revealed that Matheson and Nichols (*9*) observed a reduction of carbon tetrachloride on their cathode-ray oscillograph used in conjunction with the usual polarographic arrangement. Robinson (*11*) states that a clear wave for carbon tetrachloride in methanol was obtained at an $E^1/_2$ of −1.45 volts *vs.* S.C.E. with a cathode-ray oscillograph in the polarographic circuit. Attempts at this laboratory to purify the carbon tetrachloride by distillation, adsorption, and acid and alkali treatment all resulted in products with the same polarographic characteristics. This phenomenon should probably be investigated further.

Table VI. Linearity of Diffusion Current *vs.* Concentration of Acetaldehyde

(Wave measured by two methods)

Acetaldehyde, Mg./50 Ml. (*C*)	Wave Height, μa. (i_d) Extrapoloted method	Wave Height, μa. (i_d) Fixed potential method	i_d/c Ext.[a]	i_d/c F.P.[b]
1.23	3.07	3.42	2.50	2.78
2.45	6.35	6.92	2.59	2.82
6.13	15.51	17.16	2.53	2.80
		Av. 2.54 ± 0.03		2.80 ± 0.01

[a] Extrapolation.
[b] Fixed potential.

It was decided therefore to substitute benzene, which also has desirable characteristics in such a study. Preliminary tests showed that benzene made no contribution to the diffusion or residual currents of any of the aldehyde investigated.

Effect of Measurement of Wave Height. The precision demanded by this analysis is higher than is usually obtained in polarographic work. Temperature control, volume dilution, etc., received careful consideration in the early phase of the work and need no further elaboration. The value for the diffusion current, however, varied considerably depending on the method used. Taylor (*14*) presented a critical evaluation of different methods of measuring the diffusion current. Pilot ion and other comparative techniques were not used here because of the "crowded" polarograms due to the double reduction wave of oxygen which preceded the aldehyde waves. An absolute method was difficult because the aldehyde residual current could not be exactly evaluated, owing to the omnipresent oxygen. Best results were finally obtained by compensating the oxygen waves to a low but constant value and starting the polarogram at this point. The residual and limiting currents were measured at fixed potentials and the difference between the two was taken as the diffusion current. To this end it was found that the Sargent Model XXI polarograph was more precise than the Model XX, presumably because of the inherent limitations of a continuous Ayrton shunt and the better control of the down-scale compensator in the later unit. Table VI shows the results obtained using two methods of measuring wave height. In the first, the extrapolation technique, both the residual and limiting currents are extrapolated until they intercept an extrapolated line of the ascending portion of the wave. The difference between the points of interception is the diffusion current. The second method, the fixed potential technique, is described above.

Table VII. Effect of Supporting Electrolyte on Additivity of Diffusion Currents from Mixtures of Acetaldehyde and Propionaldehyde

Acetaldehyde, Mg./50 Ml.	Propionaldehyde, Mg./50 Ml.	i_d, Mm. LiOH 0.1 *M*	i_d, Mm. Li_2SO_4 0.05 *M*	i_d, Mm. LiCl, 0.1 *M*
1.36	...	58	56	55
2.72	...	117	112	111
1.36	1.46	92	103	101
...	1.46	45	44	45
2.72	1.46	151	159	155

The use of the fixed potential method results in a better constancy for $K(i_d/C)$. The residual current for the aidehyde waves is flat and the use of precision helipots to control the upscale and down-scale settings of the pen makes possible very reproducible compensation for the oxygen waves. The potential pair used in this study were −1.60 and −1.975 volts *vs.* S.C.E. The full damping capacitance was used in all measurements. Using the fixed potential method the K value for propionaldehyde was found to be 2.07 ± 0.01 and for *n*-butyraldehyde 1.56 ± 0.01.

Effect of Supporting Electrolyte on Diffusion Current of Mixtures of Aldehydes. Lithium hydroxide has frequently been recommended as a supporting electrolyte for the polarographic determination of mixtures of aldehydes (*6*, *13*, *16*). Because of the exploratory nature of this work, a study was made of the effect of lithium hydroxide, lithium sulfate, and lithium chloride on the additivity of the diffusion currents of the different aldehydes when present in mixtures. It became apparent at once that lithium hydroxide in concentration from 0.5 to 0.001 *M* invariably resulted in diffusion currents which are smaller than the sum of the individual diffusion currents. Table VII shows some results of these experiments.

On the basis of the results in Table VII either lithium chloride or lithium sulfate would be satisfactory. Mixtures of formaldehyde and acetaldehyde studied polarographically in this laboratory showed mutual suppression of the diffusion currents in dilute lithium hydroxide, none in neutral medium. The cause is presumably a condensation catalyzed by hydroxyl ion.

Determination of Extraction Coefficients (α). The extraction coefficient, α, for each of the aldehydes was determined by the method described above. Ten-milliliter quantities of aqueous solutions and benzene were usually used in the extractions. The values were obtained over a broad enough concentration range to establish an adherence to or departure from constancy of α with change in concentration.

In terms of per cent deviation, *n*-butyraldehyde shows the poorest results. This is probably due to two factors: (1) the small wave resulting when low concentrations of *n*-butyraldehyde are extracted because of the low α value and (2) the relatively steeper slope of the limiting current of *n*-butyraldehyde com-

Table VIII. Extraction Coefficients of Acetaldehyde, Propionaldehyde, and *n*-Butyraldehyde

Aldehyde	Concn., Mg./Ml.	α
Acetaldehyde	7.60	0.749
	3.80	0.735
	1.90	0.735
	0.95	0.742
	0.47	0.742
		Av. 0.741 ± 0.004
Propionaldehyde	7.00	0.321
	3.50	0.326
	1.70	0.319
	0.85	0.322
	0.42	0.325
		Av. 0.323 ± 0.002
n-Butyraldehyde	8.90	0.094
	4.45	0.089
	2.22	0.095
	1.11	0.090
	0.55	0.098
		Av. 0.092 ± 0.003

pared to acetaldehyde and propionaldehyde. Continued checking of the α values for *n*-butyraldehyde did nothing to increase the precision. It is likely that in this case a smaller value of V_s/V_w should have been employed in the measurement and the value of V_s/V_w computed for $V_s/V_w = 1$ from Equation 2.

FURTHER STUDIES

Analysis of Binary Systems. A series of binary mixtures of aldehydes in water was prepared. After an aliquot of the solution was analyzed polarographically, another aliquot, usually 10 ml., was extracted with an equal volume of benzene as described above and an aliquot of the aqueous layer was again run polarographically. The diffusion currents were corrected where necessary to the same aliquots for both analyses.

In order to simplify the computations to follow, the calculations will be based on solving i_d (diffusion current) rather than concentration. The general form for the three analyses to follow is:

$$X_A + Y_B = i_0$$
$$\alpha_A X_A + \alpha_B Y_B = i_1$$

where X_A = wave height, μa., for component A
Y_B = wave height, μa., for component B
i_0, i_1, α_A, and α_B have been previously described.

ACETALDEHYDE–PROPIONALDEHYDE. Mixture contained 0.613 mg. per ml. of acetaldehyde, and 0.947 mg. per ml. of propionaldehyde. Two milliliter aliquots were run before and after extraction with benzene.

X = diffusion current, μa., due to acetaldehyde in 2-ml. aliquot
Y = diffusion current, μa., due to propionaldehyde in 2-ml. aliquot
$X + Y = 7.35\mu a.$
$0.741X + 0.323Y = 3.80\mu a.$
Solving: $X = 3.41\mu a.$ = 0.609 mg. per ml. (0.613 mg. per ml. = known value for acetaldehyde)
$Y = 3.94\mu a.$ = 0.951 mg. per ml. (0.947 mg. per ml. = known value for propionaldehyde)

ACETALDEHYDE–*n*-BUTYRALDEHYDE. Mixture containing 0.613 mg. per ml. of acetaldehyde and 0.316 mg. per ml. of *n*-butyraldehyde. Five-milliliter aliquots were run before and after extraction.

X = diffusion current, μa., due to acetaldehyde in 5-ml. aliquot
Y = diffusion current, μa., due to *n*-butyraldehyde in 5-ml. aliquot
$X + Y = 11.04\mu a.$
$0.741X + 0.0908Y = 6.60\mu a.$
Solving: $X = 8.61\mu a.$ = 0.625 mg. per ml. (0.613 mg. per ml. = known value for acetaldehyde)
$Y = 2.43\mu a.$ = 0.312 mg. per ml. (0.316 mg. per ml., = known value for *n*-butyraldehyde)

PROPIONALDEHYDE–*n*-BUTYRALDEHYDE. Mixture containing 0.947 mg. per ml. of propionaldehyde and 0.316 mg. per ml. of *n*-butyraldehyde. Five-milliliter aliquots were used for determining both i_0 and i_1 values.

$X + Y = 12.20\mu a.$
$0.322X + 0.0908Y = 3.42\mu a.$
Solving: $X = 9.99\mu a.$ = 0.966 mg. per *ml. (0.947* mg. per ml. = *known* value for propionaldehyde)
$Y = 2.21\mu a.$ = 0.284 mg. per ml. (0.316 mg. per ml. = known value for *n*-butyraldehyde)

The poorer accuracy for the propionaldehyde–*n*-butyraldehyde mixture is to be expected, inasmuch as the *n*-butyraldehyde diffusion current accounted for a small fraction of the total diffusion current (concentration effect of Figure 2) and the α values for propionaldehyde and *n*-butyraldehyde are closer together than the other two pairs of α values—i.e., $\alpha_A^n - \alpha_B^n$ is small. This then serves to point up a potential source of error in the method as described: When component B is very minor in concentration compared to A, the inherent error in the determination of the i_0 and/or i_1 value may be of a magnitude to cause a gross error in B while resulting only in minor error in A. Ways to reduce these difficulties have been discussed above and in another paper (*15*) and it may suffice to mention here that changes in V_s/V_w, n, or extraction solvent for a given solute pair to cause the widest possible difference in partition constants should be studied as outlined above to minimize such errors.

Analysis of Ternary Mixture. A mixture of acetaldehyde (0.306 mg. per ml.), propionaldehyde (0.473 mg. per ml.), and *n*-butyraldehyde (0.316 mg. per ml.) in water was prepared. Five milliliter aliquots were run to obtain i_0 and i_1, and a 10-ml. aliquot for i_2 in an attempt to minimize the loss in accuracy because of the small wave. This, of course, entailed an initial extraction of 20 ml. of the aqueous solution and a second extraction of 12 ml. of the aqueous layer from the first extraction.

The results were all computed on a 5-ml. aliquot basis.

$i_0 = 11.68\mu a.$ Let X = wave height in μa. due to acetaldehyde
$i_1 = 4.92\ \mu a.$ Let Y = wave height in μa. due to propionaldehyde
$i_2 = 2.89\mu a.$ Let Z = wave height in μa. due to *n*-butyraldehyde

The equations are:

$$X + Y + Z = 11.68$$
$$0.714X + 0.322Y + 0.0908Z = 4.92$$
$$(0.741)^2X + (0.322)^2Y + (0.0908)^2Z = 2.89$$

Solving: $X = 4.40\mu a.$ = 0.315 mg. per ml. (0.306 mg. per ml. = known value for acetaldehyde)
$Y = 4.31\mu a.$ = 0.416 mg. per ml. (0.473 mg. per ml. = known value for propionaldehyde)
$Z = 2.97\mu a.$ = 0.383 mg. per ml. (0.316 mg. per ml. = known value for *n*-butyraldehyde)

Table IX. Comparison of Experimental and Predicted Errors

Blend	Component	Concentration, Mg./Ml. Known	Found	% Error, Found	Error, % Amount Present, Computed: 1% error in i_0, i_n	0.2% error in i_0, i_n
1	Acetaldehyde	0.613	0.609	−0.58	±2.9	±1.1
	Propionaldehyde	0.947	0.953	+0.51	4.3	1.3
2	Acetaldehyde	0.613	0.615	+0.35	3.5	0.80
	n-Butyraldehyde	0.316	0.312	−1.23	6.9	2.69
3	Propionaldehyde	0.947	0.965	+1.94	1.7	1.7
	n-Butyraldehyde	0.316	0.284	−10.1	8.0	3.7
4	Acetaldehyde	0.306	0.314	+2.8	4.3	...
	Propionaldehyde	0.473	0.416	−12.0	20.0	...
	n-Butyraldehyde	0.316	0.382	+20.7	29.0	...

One can readily perceive the gross errors in this analysis for a ternary system. The sensitivity to small errors in i becomes even more obvious when one calculates the "true" values for i_0, i_1, and i_2.

i_0
$0.306 \times 5 \times 2.80 = 4.28\mu a.$ for acetaldehyde (X)
$0.473 \times 5 \times 2.07 = 4.90\mu a.$ for propionaldehyde (Y)
$0.316 \times 5 \times 1.56 = 2.46\mu a.$ for *n*-butyraldehyde (Z)
Total 11.64μa., calculated value

i_1
0.741 (4.28) + 0.322 (4.90) + 0.0908 (2.46) = 4.97μa., calculated value
i_2
$(0.741)^2(4.28)$ + $(0.322)^2(4.90)$ + $(0.0908)^2(2.46)$ = 2.88μa., calculated value

Thus an error of +0.34% in i_0, of −1.01% in i_1, and of −0.34% in i_2 resulted in errors of +2.8% in the acetaldehyde determination, −12.0% in the propionaldehyde determination, and +20.7% in the *n*-butyraldehyde determination.

DISCUSSION OF LIMITATIONS AND ADVANTAGES

The results of these experiments have been summarized in Table IX.

The results of the first two analyses are seen to be considerably better than would have been expected. It is dangerous to draw many conclusions from so few data, in the light of the statistical nature of the computations of error, but it would seem that the calibration data are somewhat better than indicated by the precision of the data of Table VI and IX and that the diffusion currents have been measured to better than 1% in all cases. It seems possible that the back-extraction technique proposed by Tsai and Fu (*15*) might be used to increase the precision of determining the components which are preferentially extracted. A more attractive alternative involving less manipulation, which has not been investigated, is the possibility of measuring the extracted component in the organic phase. If possible experimentally, this would result in greatly improved precision for the extracted component and have the advantage over the back-extraction technique of reducing the number of experimental steps. Nonconstancy of α *vs.* C should not be considered a deterrent in the use of partition polarography as an analytical tool. If a smooth curve for α *vs.* C can be obtained with good precision, a method of calculation for C when α is not definitely known is available (*2*). This is the method of successive approximations and briefly would involve the following steps in a binary system.

1. Obtain i_0 and i_n as described
2. Assume values for α_A and α_B
3. Solve for C
4. Using the values for C, obtain from the plots of α_A *vs.* C_A and α_B *vs.* C_B new values for α_A and α_B
5. Solve for C again
6. Continue until there is no significant variation in C in two successive solutions

The general method described above can, of course, be applied to the analysis of any homologous series where sufficient spread between α values can be achieved by proper choice of solvents and where a precise method for measuring the total components in one of the layers has been developed. The major advantage is, of course, the fact that such an analysis is now polarographically possible. In addition, the time required for a binary system is usually short, 15 to 20 minutes, in contrast to many hours by the usual chemical procedures.

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Mobile Infrared Spectrometer

For Rapid, on-the-Spot Analyses

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THE development of the modulated beam type of infrared spectrometer has permitted the operation of this instrument under conditions of fairly widely ambient room temperatures without any appreciable drift of the instrument zero point. A little-realized value of this property is that it now permits the analyst to set up his instrument for on-the-spot analyses at the location of the chemical experiment. This is especially important where the critical steps in the experiment involve reactions in the gaseous state or where they may be followed by the observation of changing compositions of gaseous mixtures. Heretofore, the chemist was required to withdraw samples from his reaction system periodically and send them to the spectroscopy laboratory for analysis.

To eliminate this transfer of material and its associated delays when the infrared spectral absorption was the basis of the analysis, the infrared gas analyzers (*5*) and, more recently, a multicomponent analyzer (*4*) were developed. Neither of these methods, however, fulfills the requirement of versatility when the various intermediates or by-products of a reaction are unknown. The mobile unit herein described was developed for the purpose of providing rapid, on-the-spot analyses involving any region of the infrared spectrum normally covered. Because it is essentially a spectrometer, either spot checks of the concentration of several components may be made or a continuous record may be obtained of the concentration of a single component.

SETUP OF INSTRUMENT

Basically, the instrument consists of a Perkin-Elmer Model 12C spectrometer which, along with all the necessary electrical

and optical components, has been mounted as a single unit on a mobile carriage. In addition to the standard facilities supplied with the instrument, there has been added a means of rapidly determining absorbance values without recourse to calculations. No complete description of this instrument exists in the literature, but a description of the optical system (*1*) and of a somewhat modified electrical system (*3*) may be found. Detailed descriptions are given in the manufacturer's bulletins.

The physical and electrical layouts are illustrated in Figure 1, which shows the locations of the various elements of the complete unit.

ing and chassis were made electrically common and a separate ground lead was included in the main power cable.

Several changes were made on the original equipment, including the addition of a null-balance circuit similar to the one in use on the earlier model of the Perkin-Elmer spectrometer (*2*) in this laboratory and some modifications of the recording system. The normal power supply for the globar consisted of a Sola voltage-regulating transformer and a Powerstat. By introducing a Variac before the Sola and operating on a power plateau, some added source stabilization was obtained. Checks on the noise level of the unit indicated that the peak-to-peak noise was about

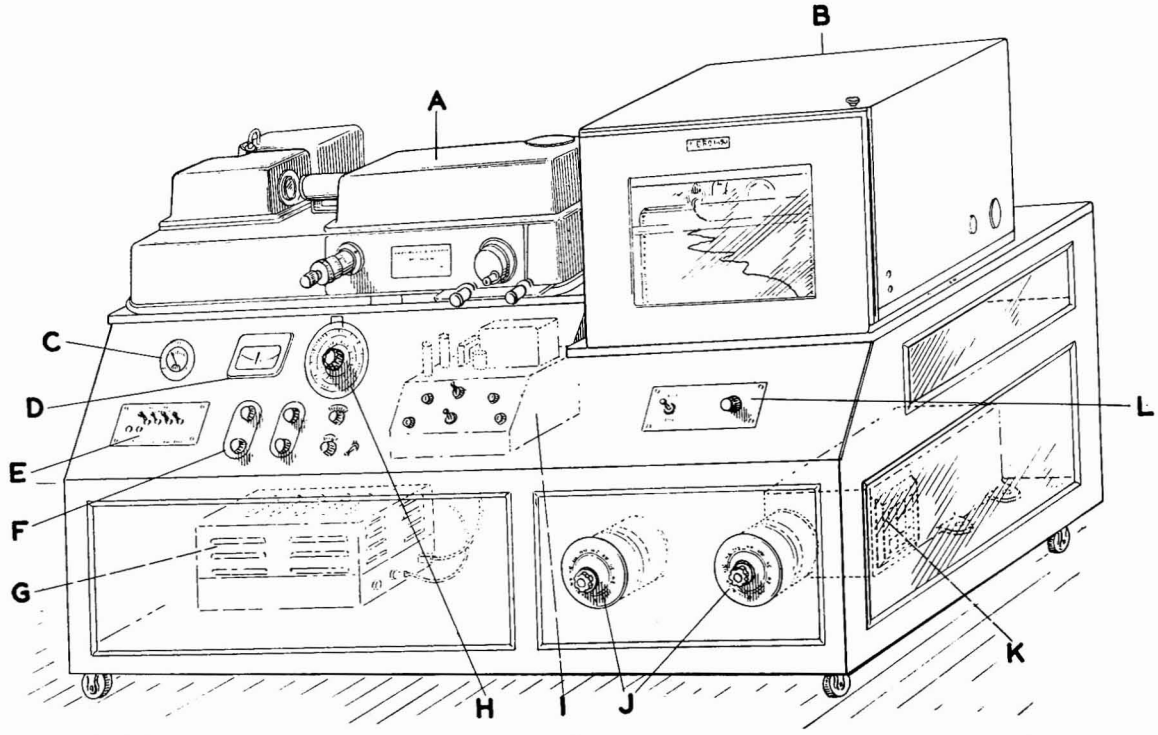

Figure 1. Phantom Drawing of Complete Mobile Spectrometer Unit Showing Location of Component

A. Spectrometer	*G.* Amplifier power supply
B. Recorder	*H.* Null circuit potentiometer
C. Wattmeter for Globar	*I.* Amplifier
D. Galvanometer	*J.* Variac and powerstat
E. Recording system controls	*K.* Sola voltage regulator
F. Null circuit controls	*L.* Filter circuit controls

The framework consists of 2 × 2 inch pine, trussed at the front and back with airplane cable, while the sides, top, and shelves are five-ply plywood panels to aid in strengthening the structure. Aluminum panels, hinged at the bottom, provide space for the controls with easy accessibility of the elements behind them. The carriage is mounted on locking casters which serve as legs when the instrument is in use. A detachable notebook shelf is also included to serve as a convenience to the operator, as is shown in Figure 2. This, along with other supplementary equipment such as absorption cells, cell holders, and the like, may be stored in a compartment beneath the recorder. The smaller aluminum panel serves as a door for this compartment and also as a mount for the response controls of the filter circuit. One electrical outlet plus water and sink facilities is needed for operation. The entire unit measures 2 feet, 2 inches by 4 feet, 8 inches and is 3 feet, 2 inches high, a size which permits passage through standard door frames.

In order to minimize pickup, the amplifier was placed as far as possible from the two power supplies and, in particular, the Sola voltage stabilizer. For this reason also the thermocouple lead was kept as short as possible, although it was still found necessary to wrap it with Mu metal strips for further shielding. The interconnections were made with shielded cable using airplane-type connectors for flexibility and easy maintenance. All cable shield-

Figure 2. Mobile Spectrometer Unit Showing Detachable Notebook Shelf in Place

A compact mounting containing the Perkin-Elmer Model 12C infrared spectrometer complete with the necessary power supplies, amplifier, and recorder is described. Also included is a null-balance circuit, the use of which enables the operator to obtain absorbance values directly without recourse to calculations. The entire unit is mounted on casters to facilitate the performance of infrared analyses at the site of the laboratory experiment.

10×10^{-9} volt, a value sufficiently close to the recommended 8×10^{-9} volt for normal operation. Because it was desired to operate the instrument with a null-balance densitometer circuit in conjunction with either a modulated or unmodulated beam, a sixteen-pole, three-position switch was included for the purpose of making the necessary circuit changes.

The advantage of the incorporation of the null-balance circuit is most apparent in routine analyses where all the components of the mixtures being analyzed are known. With it the operator is able to read the appropriate absorbance values directly from a scale attached to the potentiometer of a voltage dividing circuit used to buck out the thermocouple signal before amplification. A simple galvanometer connected to the output of the amplifier serves to indicate the null condition. In the further interest of speed and ease of operation, the controls required for this circuit were located under the sample space and slit control of the spectrometer, thereby making them readily accessible.

Because of the modulation of the beam in the Model 12C instrument, it was necessary to introduce the bucking voltage of the null circuit at such a point in the amplifier that it as well as the zero control and test signal would be interrupted in phase with the beam modulation. It was further required that the null circuit should not interact with either the positioning or polarity of the zero balance control.

To accomplish these purposes it was necessary to introduce a second 1.5-volt battery and use both poles of the double-pole, single-throw switch individually. The modified amplifier circuit is shown in Figure 3. Normally, in the case of modulated beam operation, the "dark current" is zero and the direct current feed-back circuit of the filter unit is used to compensate for the thermocouple direct current signal. However, an overdamping of the galvanometer occurred when this filter unit was used with the null circuit, and other means had to be found to compensate for this thermocouple signal to prevent its appearance as an alternating signal superimposed on the rectified amplifier output.

This was accomplished by disconnecting the zero balance leads from the switch on the modulator shaft and shorting out terminals 1 and 2 of the amplifier, thus supplying an adjustable direct current voltage sufficient to buck out the direct current thermocouple signal before amplification. The necessary circuit changes were made by use of the selector switch, S_1, shown in the switching circuit given in Figure 4. Reading clockwise, position 1 of this switch was chosen for the normal operation of the spectrometer, and 2 and 3 for the unmodulated and modulated beam operation of the null-balance unit, respectively.

The voltage divider, which again is an integral part of the Perkin-Elmer filter, also had to be replaced in the null circuit and, as indicated in Figure 4, it was done by using a variable 1000-ohm potentiometer, R_{10}, the center tap of which was grounded, having a 950-ohm fixed resistor at each end to give a finer control in its adjustment. The balance of the system may be checked by introducing a standard direct current

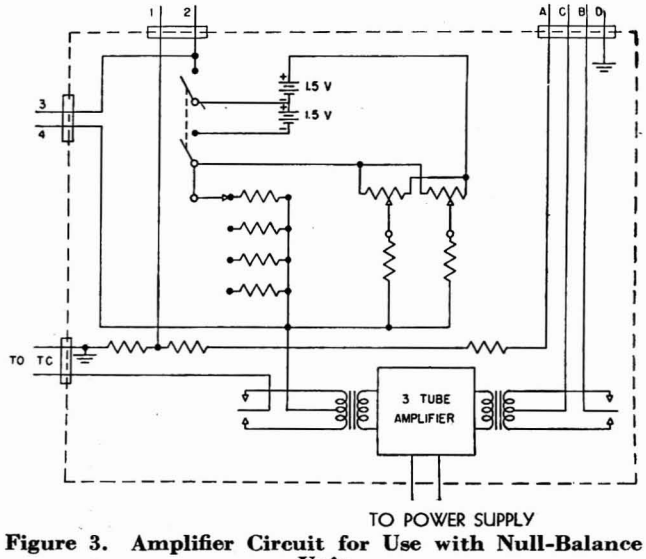

Figure 3. Amplifier Circuit for Use with Null-Balance Unit

signal as from the test micro-volts and adjusting the potentiometer until the galvanometer pointer is at its mechanical zero. The slight ripple which remains during operation, causing a flickering of the galvanometer, was minimized by placing a 500-mfd. condenser across the galvanometer terminals. A fair but not objec-

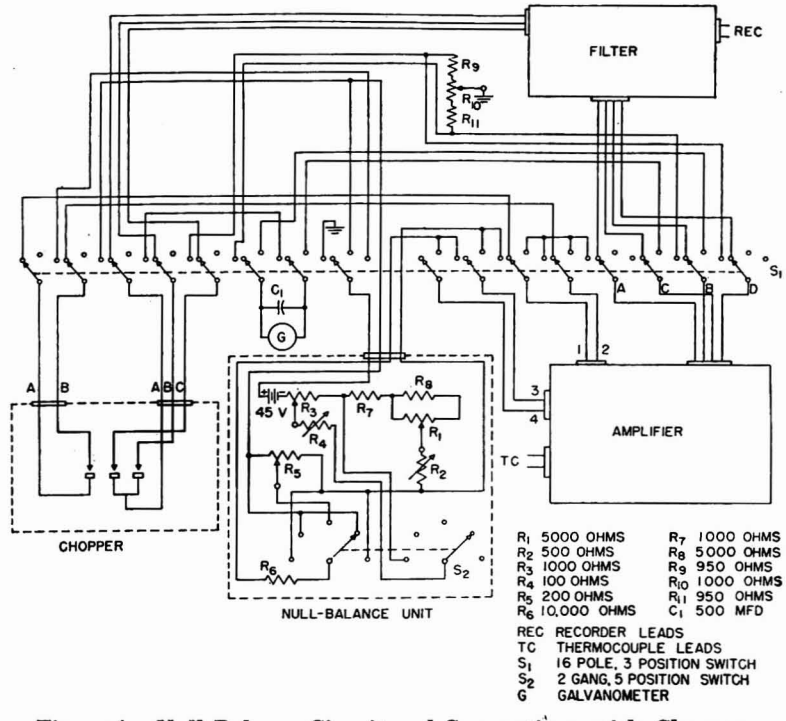

Figure 4. Null-Balance Circuit and Connections with Chopper, Amplifier, and Filter Units

tionable amount of sluggishness of the galvanometer was caused by the introduction of this condenser. When the unit was operated with an unmodulated beam, this sluggishness was not often apparent because of the much higher signal levels normally encountered.

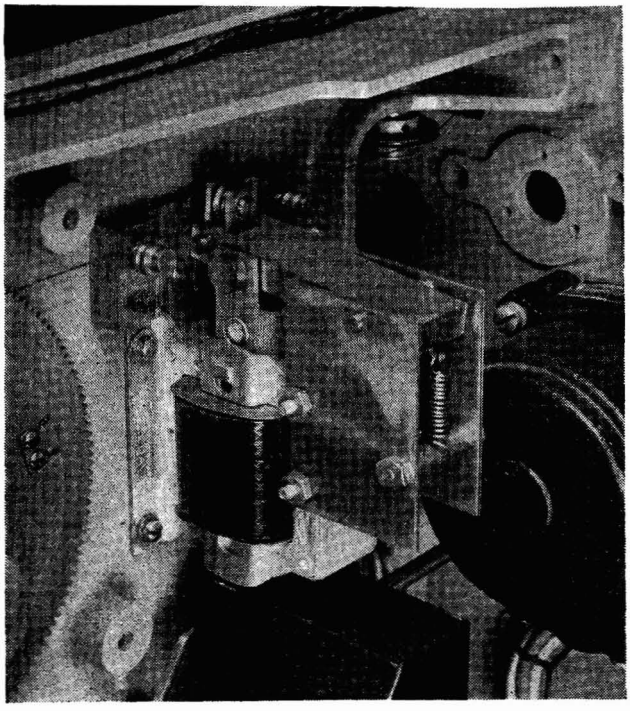

Figure 5. Clicker Unit for Producing Fiducial Marks on Recorder Chart

Because a current flows in the null-balance circuit when it is set at the galvanometer null point, the angular displacement of the potentiometer, R_5, is not a linear function of the transmittance. This, of course, could be compensated for by using a nonlinear scale but, because this nonlinearity was found to amount to less than 0.6%, a linear scale was used satisfactorily. An inexpensive potentiometer was used, so adjusted that the runoffs at the ends did not produce any discontinuity in the resistance. When tested, it was found that the nonlinearity of this potentiometer did not exceed ±0.2%.

The original system for placing fiducial marks on the recorder chart was less satisfactory than was desired because the pen would not quickly return to the spectral curve after its excursions. A better system consists of a solenoid arranged to give a sudden jerk to the pen cable of the recorder. This solenoid is operated by the discharge of a condenser whose capacity is such that the release is instantaneous. Figure 5 is a photograph of the back of the hinged element of the Brown recorder showing this unit, and the circuit is given in Figure 6.

Two other minor alterations were made in line with the operational procedures used in this laboratory. Because portions of the spectral tracings are normally removed from the recorder as soon as they are completed, it was convenient to make the recorder door easily removable rather than to leave it open. To accomplish this the light wires and bracket were removed from the door and the upper hinge pin was replaced with a removable one having a knob on its upper end. Again, it has been found convenient to divide the rock salt spectrum into six sections and to use four successive scanning speeds. In order to obtain satisfactory spectra in a minimum of time, the over-all speed of the Perkin-Elmer motor drive was almost doubled by the simple substitution of two gears in the gear train of the motor drive unit.

Since this installation was made the Perkin-Elmer Corporation has developed an improved amplifier and detector system. In this the beam is chopped to produce a *13-cycle modulation* and the output of the thermocouple is fed through a short lead to a preamplifier. This serves to increase the signal by a factor of about 10,000 before it is transmitted to the main amplifier, thereby minimizing noise from extraneous impulses and stray 60-cycle signals and rendering the instrument more favorable for operation in "noisy" locations. The essential parts of this system are used in the newer Perkin-Elmer Model 12C instrument (*3*). The use of this amplifier is, therefore, to be recommended over the breaker-type amplifier used in the instrument described herein.

OPERATION OF NULL-BALANCE CIRCUIT

Referring to Figure 4, with S_1 in position 2, reading clockwise, the dark current present in unmodulated beam operation is compensated for by the balance control on the amplifier panel with the switch, S_2, in position 4, and the shutter closed. All other operations are the same for modulated or unmodulated beam operation. The voltage span of the potentiometer, R_5, equivalent to 100% transmittance, is obtained by adjusting the coarse and fine variable resistors, R_1 and R_2, or the slit width with S_2 in position 5 and the shutter open. The sample cell is then placed in the beam and the potentiometer, R_5, is adjusted to reproduce the null position of the galvanometer with S_2 in position 3. The fraction of the slide-wire thus utilized is proportional to the per cent transmittance.

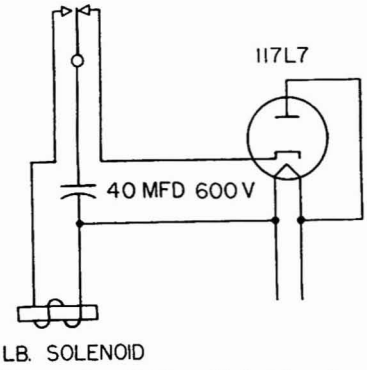

Figure 6. Clicker Unit Circuit

The range of transmittance spanned by the potentiometer slide wire can be decreased for measuring small differences in relatively high absorbances by making the slit wider than normal and adjusting the coarse and fine variable resistors, R_3 and R_4, with S_2 in position 1 when making the cell-out adjustment. After this first adjustment of the resistors R_3 and R_4, the operations are similar to those in the preceding paragraph except that S_2 is moved to position 1 rather than 5 for each cell-out adjustment. Switch positions 2 and 4 are identical for convenience when a span of less than 100% transmittance is used.

ACKNOWLEDGMENT

The authors wish to express their gratitude to Max D. Liston and other members of the Perkin-Elmer Corporation for their advice in the design of this unit and the electrical circuits involved. They also thank Charles Salzman of these laboratories for his aid in rewiring the amplifier.

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Infrared-Mass Spectrometer Combination Method for Light Hydrocarbon Analysis

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A method is presented for the complete analysis of C_1 to C_4 paraffin–mono-olefin hydrocarbons (including differentiation of *cis*- and *trans*-2-butene) without the usual low temperature distillation or other separation methods. A simple total pressure computation allows all components (including total butenes) to be based upon mass spectrometer data and the butene split to be made by means of infrared data. The resulting analysis takes advantage of the superior infrared accuracy for butenes and retains the accuracy and wide range of applicability of the mass spectrometer to other light hydrocarbons.

THE use of infrared spectrometry and mass spectrometry individually in the analysis of various hydrocarbon mixtures has been covered thoroughly in previous publications (*1–3, 5, 8, 9*). A method has been described (*6*) for the combination of data from both infrared and mass spectrometers in which only 1-butene and isobutene (2-methylpropene) splits are obtained; empirical pressure correction factors are introduced to compensate for instrument fluctuations to derive an absolute basis for the computation. The combination method of analysis employed in this laboratory differs from that described (*6*) in several significant respects: The present method employs a simple total pressure computation to derive an absolute basis for the combination calculation; the normalization procedure is different in that a simple correction on the butenes can be made once the mass spectrometer data have been made absolute; and the components determined by infrared are different.

In order to obtain a complete isomeric analysis for butenes in C_1 to C_4 hydrocarbon mixtures, it is generally necessary to perform a low temperature distillation to segregate the butanes and butenes for subsequent infrared analysis (*2*). The resulting analysis yields values for all the butene isomers, including *cis*- and *trans*-2-butene. The mass spectrometer can be used to obtain a comparable analysis, except that the *cis*- and *trans*-2-butene isomers cannot be distinguished and thus a total 2-butene analysis must be made. Furthermore, the mass spectrometer analysis for these isomeric butenes is far less accurate than for the other hydrocarbon components, and is also inferior to that obtained by the usual distillation-infrared technique. The inaccuracies involved in the butene analysis by mass spectrometer range from 1.0 to 4.0 mole %, depending upon the concentration ranges and extent of drifts in instrument calibrations. Milsom *et al.* (*6*) use infrared data to determine isobutane (2-methylpropane) and isobutene and mass spectrometer data for *n*-butane and 1-butenes. Starr and Lane have shown (*7*) the mass spectrometer to be equal or superior to the infrared for the analysis of all components in this range except the butene isomers. The total butene value was shown to be accurate by the mass spectrometer, whereas the infrared was of considerably greater accuracy in the determination of the individual components. Thus it appeared that a logical technique would be to utilize the superior infrared butene accuracy and the extended range of the mass spectrometer in one method to arrive at data comparable to those obtained by the more time-consuming method of low temperature distillation and subsequent infrared determination.

APPARATUS

The mass spectrometer used was a Model 21-102 instrument manufactured by the Consolidated Engineering Corporation,

Table I. Infrared Calibration Coefficients[a] (Beckman IR-1)

Wave Length, μ	Pressure, Mm. Hg	Methane	Ethene	Ethane	Propene	Propane	Iso-butane	*n*-Butane	1-Butene	*cis*-2-butene	*trans*-2-butene	Iso-butene	Iso-pentane	*n*-Pentane
9.05	570	0.001	0.180	0.011	0.094	0.030	0.026	0.047	0.595	0.135	0.119	0.118	0.044	0.062
10.4	40	0.000	0.235	0.010	0.235	0.004	0.002	0.086	0.116	0.150	0.724	0.005	0.041	0.004
11.4	55	0.000	0.154	0.040	0.228	0.015	0.004	0.001	0.111	0.016	0.017	0.562	0.002	0.034
14.4	70	0.000	0.011	0.002	0.015	0.011	0.011	0.020	0.037	0.636	0.008	0.014	0.011	0.021

[a] Corrected absorbance at unit mole fraction.

Table II. Mass Spectral Sensitivity Coefficients of C_1–C_5 Hydrocarbons

(Divisions/micron pressure)

Mass	*n*-C_5H_{12}	*i*-C_5H_{12}	ΣC_5H_{10}	*n*-C_4H_{10}	*i*-C_4H_{10}	i-C_4H_8	1-C_4H_8	2-C_4H_8	C_3H_8	C_3H_6	C_2H_6	C_2H_4	CH_4	N_2	O_2	H_2
2	...	...	1.10	0.75	0.60	0.95	0.90	0.78	0.92	0.81	1.86	1.31	1.09	...	...	126.3
16	0.62	1.07	1.20	0.61	1.38	0.48	0.59	0.58	0.98	0.64	0.86	0.47	245.3	...	38.20	...
28	29.72	19.25	21.57	131.9	13.94	70.30	101.6	100.32	191.5	3.34	380.7	278.8	...	276.3	...	...
30	2.47	2.94	2.29	3.93	0.69	1.79	1.89	2.09	7.16	0.06	90.06	0.12	...	...	...	...
32	1.84	1.92	...	1.42	...	...	...	...	...	...	...	...	...	...	220.9	...
42	266.6	252.9	243.2	49.88	154.7	12.48	12.15	10.81	19.50	169.5	...	...	...	...	...	...
43	468.3	301.9	11.37	413.1	480.4	0.36	0.56	0.38	77.54	5.61	...	...	...	...	...	...
44	15.21	9.78	...	13.48	15.61	...	0.03	0.03	93.35	0.12	...	...	...	...	...	...
56	10.24	50.22	13.26	3.23	1.81	156.2	138.7	164.4	...	...	...	...	...	...	...	...
57	61.30	169.1	0.52	10.36	14.58	7.63	5.98	6.94	...	...	...	...	...	...	...	...
58	2.78	7.39	...	50.44	12.19	0.22	0.14	0.17	...	...	...	...	...	...	...	...
70	0.45	0.33	121.8	...	...	...	...	...	...	...	...	...	...	...	...	...
72	41.13	18.54	0.14	...	...	...	...	...	...	...	...	...	...	...	...	...

Table III. Total Pressure Matrix

(Fractional coefficients, computer solution, and total pressure equation)

		1	2	3	4	5	6	7	8	9	10	11	12	*M*
Factor		126.3	245.3	380.7	90.96	266.6	153.1	93.35	480.4	50.44	41.13	169.1	121.8	
Mass		2	16	28	30	42	56	44	43	58	72	57	70	
1	H_2	1.0000	...	...	...	...	...	...	...	...	...	...	...	0.5
2	CH_4	0.0086	1.0000	...	...	...	...	...	...	...	...	...	...	0.5
3	C_2H_4	0.0104	0.0019	0.7323	0.0013	...	...	...	...	...	...	...	...	0.5
4	C_2H_6	0.0147	0.0035	1.0000	1.0000	...	...	...	...	...	...	...	...	0.5
5	C_3H_6	0.0064	0.0026	0.0088	0.0007	0.6358	...	0.0013	0.0117	...	...	...	...	0.5
6	ΣC_4H_8	0.0070	0.0022	0.2403	0.0212	0.0446	1.0000	0.0003	0.0009	0.0036	...	0.0405	...	0.5
7	C_3H_8	0.0073	0.0040	0.5029	0.0787	0.0732	...	1.0000	0.1614	...	...	...	...	0.5
8	i-C_4H_{10}	0.0047	0.0056	0.0366	0.0076	0.5803	0.0118	0.1672	1.0000	0.2417	...	0.0862	...	0.5
9	n-C_4H_{10}	0.0059	0.0025	0.3465	0.0432	0.1871	0.0211	0.1444	0.8498	1.0000	...	0.0613	...	0.5
10	n-C_5H_{12}	...	0.0025	0.0781	0.0272	1.0000	0.0669	0.1629	0.9747	0.0551	1.0000	0.3626	0.0037	0.5
11	i-C_5H_{12}	...	0.0044	0.0506	0.0323	0.9487	0.3280	0.1048	0.6284	0.1465	0.4508	1.0000	0.0027	0.5
12	ΣC_5H_{10}	0.0087	0.0049	0.0565	0.0252	0.9125	0.0866	...	0.0237	...	0.0034	0.0031	1.0000	0.5
Computer solution		+0.5000	+0.4955	+0.6747	−0.1840	+0.7703	+0.3134	+0.1138	−0.0037	+0.1233	−0.2619	−0.2729	−0.2686	
Total pressure equation		+0.007905	+0.004040	+0.003545	−0.004075	+0.005779	+0.004094	+0.002438	−0.000015	+0.004889	−0.12735	−0.003228	−0.004409	

Pasadena, Calif. The infrared spectrophotometer employed was a Beckman IR-1 instrument manufactured by National Technical Laboratories, Pasadena, Calif. An electrical computer, Model 30-102, manufactured by the Consolidated Engineering Corporation, was employed in the solution of all matrices. The general techniques of operation of these instruments have been previously described (*1, 4, 8*).

PROCEDURE

Calibrations were obtained by standard techniques using the same pure hydrocarbons on both instruments. Four wave lengths in the infrared were used at a given standard pressure for each wave length as shown in Table I. The principal absorbers were found to obey Beer's law over the concentration range normally encountered (to about 50%). It was unnecessary in subsequent calculations, therefore, to employ correction curves for deviations from Beer's law. Calibrations at each of the four wave lengths were calculated in the usual manner (*2*) from null-type galvanometer measurements, and expressed as absorbance per unit mole fraction.

A summary of mass spectrometer calibration data is shown in Table II. The only precaution in handling of the sample was that a small sample was taken into a glass bulb for the mass spectrometer simultaneously with the filling of the infrared cell to ensure identical samples for both instruments. The mass spectra were recorded and the peak intensities at the selected mass numbers were read from the record.

METHOD OF COMPUTATION

In a combination of mass spectrometer and infrared data, both must be expressed in the same terms and a method devised for adjusting each set of data to an absolute basis. The difficulties involved in combination of two sets of unnormalized data can be illustrated by an example in which one half of the sample composition is determined by each—i.e., 50% by mass spectrometer and 50% by infrared. If, say, the mass spectrometer components computed to be 45% and the infrared to 55%, the apparent total would be 100% although the actual values were low and high, respectively, by 5%. It will thus be apparent that at least one set of the data must be computed on an absolute basis, so that final normalization can be correctly applied to only the unnormalized data.

The general expression for mass spectrometric computations is as follows:

$$\begin{aligned} A_{11}P_1 + A_{12}P_2 + A_{13}P_3 \ldots . A_{1n}P_n &= M_1 \\ A_{21}P_1 + A_{22}P_2 + A_{23}P_3 \ldots . A_{2n}P_n &= M_2 \\ A_{31}P_1 + A_{32}P_2 + A_{33}P_3 \ldots . A_{3n}P_n &= M_3 \\ A_{n1}P_1 + A_{n2}P_2 + A_{n3}P_3 \ldots . A_{nn}P_n &= M_n \end{aligned}$$

where A_{ij} is the calibration coefficient at mass i of component j; P_i is the concentration of component j; and M_i is the ion intensity at mass i. The solution of this general matrix results in the inverse or reciprocal matrix which may be expressed as follows:

$$\begin{aligned} P_1 &= I_{11}M_1 + I_{12}M_2 + I_{13}M_3 \ldots . I_{1n}M_n \\ P_2 &= I_{21}M_1 + I_{22}M_2 + I_{23}M_3 \ldots . I_{2n}M_n \\ P_3 &= I_{31}M_1 + I_{32}M_2 + I_{33}M_3 \ldots . I_{3n}M_n \\ &\vdots \\ P_n &= I_{n1}M_1 + I_{n2}M_2 + I_{n3}M_3 \ldots . I_{nn}M_n \end{aligned}$$

This inverse expression gives the concentrations, P, of components 1 through n as a linear relation of the ion intensities, M, by means of the inverse coefficients, I. When M_i is expressed as peak height (divisions) and A_{ij} as sensitivity (divisions per micron pressure), P_j is given as partial pressure; when both M_i and A_{ij} are expressed as sensitivities, P_j results in mole per cent. Although relative sensitivities, M_i, may be determined by use of the experimentally measured pressure, such sensitivity values are often in error because of instrumental fluctuations, etc. Milsom *et al.* (*6*) more nearly approximate absolute sensitivity expressions by applying an empirical correction factor determined from *n*-butane sensitivity ratios. However, this method represents only an approximation of the actual pressure, because complete stability of the mass spectrometer unit is assumed for the time elapsed between the butane sensitivity determination and the unknown determination

The point of emphasis here is that the mass spectrometer data can be expressed on an absolute basis by a simple computation. Referring to the in-

Table IV. Infrared and Mass Spectral Calibration for Mass Spectrometer–Infrared Combined Matrix

Equation	Mass or Wave Length, μ	1 n-C_5H_{12}	2 i-C_5H_{12}	3 n-C_4H_{10}	4 i-C_4H_{10}	5 1-C_4H_8	6 *cis*-2-C_4H_8	7 *trans*-2-C_4H_8	8 i-C_4H_8	9 C_3H_8	10 C_3H_6	11 C_2H_6	12 C_2H_4
1	72	41.13	18.54	...	...	...	...	...	...	...	...	...	...
2	57	61.30	169.1	10.36	14.58	5.98	6.94	6.94	7.63	...	...	...	...
3	58	2.78	7.39	50.49	12.19	0.14	0.17	0.17	0.22	...	...	...	...
4	43	468.3	301.9	413.11	480.4	0.56	0.38	0.38	0.38	77.57	5.61	...	...
5	9.05	0.062	0.044	0.047	0.026	0.595	0.135	0.119	0.118	0.030	0.094	0.011	0.180
6	14.4	0.021	0.011	0.020	0.011	0.037	0.636	0.008	0.014	0.011	0.015	0.002	0.011
7	10.4	0.004	0.041	0.086	0.002	0.116	0.150	0.724	0.005	0.004	0.235	0.010	0.235
8	11.4	0.034	0.002	0.001	0.004	0.111	0.016	0.017	0.562	0.015	0.228	0.040	0.154
9	44	15.21	9.78	13.48	15.61	0.03	0.03	0.03	...	93.35	0.12	...	...
10	42	266.6	252.9	49.88	154.7	12.15	10.81	10.81	12.48	19.50	169.5	...	...
11	30	2.47	2.94	3.93	0.69	1.89	2.09	2.09	1.79	7.16	0.06	90.96	0.12
12	28	29.72	19.25	131.9	13.94	101.5	100.3	100.3	70.30	191.5	3.34	380.7	278.8

Table V. Final Inverse[a] for Mass Spectrometer–Infrared Matrix

		1	2	3	4	5	6	7	8	9	10	11	12
Mass Wave Length, μ		28	30	42	44	11.4	10.4	14.4	9.05	43	58	57	72
1	C_2H_4	+4,063	−18,973	+1,504	−7,906	−406,406	−492,265	−437,421	−546,891	−75	−7,637	−649	−5,281
2	C_2H_6	+63	+10,745	+107	−960	−34,520	−33,149	−29,245	−30,252	+7	−772	−183	−690
3	C_3H_6	+129	−497	+6,185	+315	−71,174	−49,171	−44,025	−72,269	−2,162	+12,375	−4,947	−8,913
4	C_3H_8	...	...	+5	+10,995	...	...	−314	−336	−358	−12	...	−10
5	i-C_4H_8	−1,090	+3,701	−2,767	+1,536	+1,974,021	+144,199	+139,937	−197,311	+857	−2,753	+2,296	+3,501
6	*trans*-2-C_4H_8	−1,392	+5,585	−2,420	+2,200	+198,221	+1,591,436	+135,220	+84,034	+808	−4,492	+1,473	+4,327
7	*cis*-2-C_4H_8	+12	−68	−59	−163	−19,929	−1,934	+1,591,509	−96,134	+4	−567	+69	−326
8	1-C_4H_8	−925	+3,788	−390	+1,155	−288,612	−187,293	−220,755	+1,934,454	−12	+887	+116	−83
9	i-C_4H_{10}	−29	+112	−141	−2,224	+19,217	+14,088	+11,635	+9,748	+2,770	−21,767	−657	−27,377
10	n-C_4H_{10}	−2	...	+19	+525	...	+829	+943	+1,681	−635	+24,985	−705	+6,278
11	i-C_5H_{12}	+170	−644	+299	−41	−104,626	−79,006	−71,069	−63,193	−324	+788	+6,971	−8,549
12	n-C_5H_{12}	−76	+288	−135	+15	+47,331	+35,359	+32,075	+28,908	+146	−345	−3.148	+28,178
	Σ mole	+1,466	+4,050	+2,206	+5,433	+1,308,897	+941,160	+839,937	+884,034	+1,028	+701	+649	−8.967

[a] All coefficients multiplied by 10^{-6}.

verse expression above, it is apparent that the total pressure may be computed by summation of the individual pressures. An expression may be obtained for the total pressure by summation of the columnar inverse coefficients of common M terms:

$$\overset{n}{\Sigma}P_i = M_1 \overset{n}{\Sigma}I_{i1} + M_2 \overset{n}{\Sigma}I_{i2} + M_3 \overset{n}{\Sigma}I_{i3} \ldots . M_n \overset{n}{\Sigma}I_{in}$$

This total pressure equation may be computed without going through the complete inverse solution with subsequent summation of terms. In the normal inverse solution, employing an electrical computer, each column of the matrix is solved separately by successive substitution of unity in each M position with zero in the remainder of the M's (*4*). The explicit form of the summation equation can be obtained by simultaneous substitution of unity or a smaller number suitable for the computer in each of the M positions and solving. The resultant equation is the general solution for $\overset{n}{\Sigma}P_i$, and the $\overset{n}{\Sigma}I_{in}$ values obtained are used in all subsequent analyses. From this expression the total pressure may then be computed for any mixture simply as the sum of multiplicative terms involving the mixture peak height and the corresponding $\overset{n}{\Sigma}I_i$ term.

In the case of C_1 to C_4 hydrocarbon mixtures a satisfactory total pressure matrix includes the components hydrogen, methane, ethane, ethene, propane, propene, n-butane, isobutane, total butenes, isopentane (2-methylbutane), n-pentane, and total pentenes. This 12-equation matrix contains all possible components with the exception of air, hydrogen sulfide, carbon monoxide, and carbon dioxide. The latter two ordinarily may be ignored, as their presence usually is made improbable by the source of such mixtures. Diolefins and acetylenes were not considered, because they were not expected to be present in significant quantities. Air and hydrogen sulfide may be computed separately, if present, from their unicomponent masses (32 and 34). A total butene value is used because of the similarity of spectra. It has been found that no significant error is introduced in the total pressure calculation even when the butene concentration is above 50%. The total pentene value is included to make the method applicable to samples containing small amounts of pentenes (less than 3%) but is not intended for samples containing a large concentration of these components.

The total pressure matrix is shown in Table III as prepared from the mass spectral calibrations in Table II. The factored and transposed coefficients are shown with the factor value for each row and the M value. This matrix is set up in the computer and a solution is made according to the usual technique (*4*). The solution is shown as read from the computer as well as the final

Table VI. Comparison of Mass Spectrometer–Infrared Inverse and Graphical Solution

Component	Concentration, Mole %: Graphical solution	M.S.–I.R. inverse solution	Difference
Propene	6.3	6.5	0.2
Propane	10.5	10.4	0.1
n-Butane	30.2	30.0	0.2
Isobutane	14.7	14.6	0.1
cis-2-butene	3.6	3.6	0.0
trans-2-butene	1.9	2.0	0.1
Isobutene	8.5	8.5	0.0
1-Butene	6.0	6.2	0.2
n-Pentane	8.5	8.5	0.0
Isopentane	9.6	9.5	0.1
Pentenes	0.2	0.2	0.0
	100.0	100.0	Av. 0.09

Table VII. Infrared, Mass Spectrometer, and Mass Spectrometer–Infrared Comparison Analyses on C_4 Fractions

Component	Composition, Mole %: Infrared	Mass spectrometer	M.S.–I.R.
	Sample 1		
n-C_4H_{10}	5.8	5.4	5.4
i-C_4H_{10}	4.0	5.0	5.0
1-C_4H_8	33.9	30.7	33.8
cis-2-C_4H_8	7.5	10.4	6.7
trans-2-C_4H_8	0.6		0.6
i-C_4H_8	48.2	48.5	48.5
	Sample 2		
n-C_4H_{10}	32.1	31.2	31.2
i-C_4H_{10}	48.2	48.0	48.0
1-C_4H_8	6.3	3.9	6.6
cis-2-C_4H_8	3.0	5.9	3.0
trans-2-C_4H_8	0.0		0.0
i-C_4H_8	10.4	11.2	11.0

Table VIII. Analysis of Synthetic Mixtures

(All values in mole %)

	Mixture 1				Mixture 2				Mixture 3			
	Blend	M.S.-I.R.	M.S.	ΔM.S.	Blend	M.S.-I.R.	ΔM.S.-I.R.	ΔM.S.	Blend	M.S.-J.R.	M.S.	ΔM.S.-I.R.	ΔM.S.
Hydrogen	..	..	..	..	5.0	4.8	−0.2	−0.1	4.9	4.6	4.5	−0.3	−0.4
Methane	..	..	..	..	9.9	10.0	+0.1	+0.2	4.9	5.3	5.0	+0.4	+0.1
Ethene	..	..	..	..	5.0	4.9	−0.1	−0.1	4.9	4.7	5.5	−0.2	+0.6
Ethane	0.0	0.5	0.7	+0.7	24.9	24.4	−0.5	−0.3	4.9	5.0	4.4	+0.1	−0.5
Propene	5.0	5.0	5.5	+0.5	15.0	14.7	−0.3	−0.2	7.8	7.8	8.2	0.0	+0.4
Propane	9.8	9.5	9.9	+0.1	20.1	20.1	0.0	+0.2	9.9	10.0	10.3	−0.1	+0.4
Isobutene	5.0	6.0	2.4	−2.6	1.1	2.1	+1.0	−0.7	19.8	21.2	20.4	+1.4	+0.6
trans-2-butene	25.1	26.3	27.3	+1.2	4.0	4.6	+0.6	−2.2	4.9	5.3	10.1	+0.4	+0.3
cis-2-butene	5.0	5.3		−2.8	1.0	1.0	0.0		4.9	4.2		−0.7	
1-Butene	20.0	19.6	24.0	+4.0	2.0	0.5	−0.5	+3.2	9.9	9.1	8.6	−0.8	−1.3
Isobutane	10.0	9.4	9.9	−0.1	5.0	5.0	0.0	+0.1	9.9	9.8	9.7	−0.1	−0.2
n-Butane	5.0	4.6	4.9	−0.1	5.0	4.9	−0.1	−0.1	6.5	6.4	6.6	−0.1	+0.1
Isopentane	6.1	5.2	6.4	+0.3	1.0	0.9	−0.1	0.0	4.9	4.7	4.9	−0.2	0.0
n-Pentane	9.0	8.6	9.0	0.0	1.0	1.1	+0.1	0.0	1.9	1.9	1.8	0.0	−0.1
Average error of all components				±1.12			±0.26	±0.57				±0.34	±0.38
Average error of butenes				±3.13			±0.53	±2.03				±0.83	±0.73
Average error of all except butenes				±0.26			±0.15	±0.13				±0.15	±0.27

total pressure equation corrected for row factors and M conversion to unity. This equation may be used for any mixture of the listed components except those involving large pentene concentrations.

Thus, an equation has been derived for a relatively simple method of computing a "spectral" total pressure for use in determining absolute sensitivities. This spectral pressure is equal to the same value obtained by making a complete analysis of the mass spectrometer data and computing the theoretical pressure from the analysis. Because the use of theoretical pressure eliminates the need for subsequent normalization of the mass spectrometer components, a satisfactory closure of the data can be made by normalization of the butenes.

The total pressure as calculated above can now be used to compute mixture sensitivities which can be directly substituted in a combined matrix with corrected infrared absorbances in a straight-forward technique. This matrix is shown in Table IV. Equations 1 through 4 and 9 through 12 represent mass spectral sensitivity coefficients at the 72, 57, 58, 43, 44, 42, 30, and 28 masses for the components shown. Equations 5 through 8 represent infrared calibration coefficients (absorbance per unit mole fraction) at 9.05, 14.4, 10.4, and 11.4 microns for the same components. Table V shows the inverse for this combined array as solved by the electrical computer. Methane, hydrogen, and air are not included in the matrix. These components can be computed from the mass spectrum as residuals or by isotope correction, for their parent masses are essentially unicomponent and exhibit no absorption at the infrared wave lengths. Pentenes may be calculated by correcting mass 70 for pentanes. However, samples containing over 2 to 3% pentenes should be avoided in this method because of the large absorption by pentenes at the infrared wave lengths.

The resulting computation by use of the inverse should total a mole fraction of 1. However, if normalization is necessary, corrections should be made only on infrared components, inasmuch as the mass spectra components have been normalized by use of theoretical pressure as calculated from the $\sum^{n} P_i$ equation. The butene correction factor for normalization is calculated as follows:

$$\Sigma C_4^{=}\text{ (corrected)} = 1.00 - [\Sigma N - \Sigma C_4^{=}\text{ (uncorrected)}]$$

$$F = \frac{\Sigma C_4^{=}\text{ (corrected)}}{\Sigma C_4^{=}\text{ (uncorrected)}}$$

where

$\Sigma C_4^{=}$ = total C_4 olefins, by infrared
ΣN = total mole fraction by mass spectrometer and infrared calculations
F = correction factor for individual butenes

The resulting values represent the final analysis of the data, with each component expressed in mole fraction.

ACCURACY

A comparison can be made of results calculated from the data (as described above) with results obtained by a graphical approximation of the data. This approximation was carried out by the usual analysis of the mass spectrometer data, solving for total butenes and subsequent approximations and corrections of the infrared absorbances by use of a graphical plot of the minor absorbers at the various wave lengths. Such a comparison is shown for a C_3–C_5 mixture in Table VI. The largest deviation is 0.2% with an average value of 0.09%.

A comparison of the mass spectrometer–infrared method on C_4 fractions can be made with both the mass spectrometer method and the infrared as shown in Table VII. The infrared method is generally accepted as more accurate than the mass spectrometer on such mixtures and it is apparent that the mass spectrometer–infrared method is in good agreement with the infrared method where mass spectrometer and infrared are not in close agreement.

An indication of the absolute accuracy of the method can be obtained through the analysis of synthetic mixtures. Table VIII shows three synthetic mixtures of different relative compositions and the analysis of each by the mass spectrometer method alone and the mass spectrometer–infrared method. In the case of the first two synthetics, the butene analysis by the mass spectrometer–infrared method is considerably better than that by the mass spectrometer alone. Synthetic mixture 3 is analyzed with approximately the same degree of accuracy by both methods. The average error for butenes by the mass spectrometer–infrared method ranges from 0.5 to 0.8% as compared with 0.7 to 3.1% by the mass spectrometer. The other components vary from 0.2 to 0.5% and 0.1 to 0.3%, respectively, giving an overall average error for all components of 0.3 to 0.6% for the mass spectrometer–

Table IX. Repeatability of Analysis

	Mass Spectrometer–Infrared				Mass Spectrometer			
	1	2	3	Spread	1	2	3	Spread
Hydrogen	4.5	4.6	4.5	0.1	4.5	4.7	4.4	0.3
Methane	5.3	5.3	5.5	0.2	5.0	5.3	5.0	0.3
Ethene	4.4	4.7	4.7	0.3	5.5	5.5	5.2	0.3
Ethane	4.6	5.0	4.7	0.4	4.4	4.6	4.5	0.2
Propene	7.8	7.8	7.5	0.3	8.2	8.0	7.9	0.3
Propane	10.1	10.0	10.0	0.1	10.3	10.3	10.4	0.1
Isobutene	21.5	21.2	21.5	0.3	20.4	19.5	20.3	0.9
trans-2-butene	5.5	5.3	5.5	0.2	10.1	9.0	9.7	1.1
cis-2-butene	4.3	4.2	4.3	0.1				
1-Butene	9.3	9.1	9.2	0.2	8.6	10.3	9.5	1.7
Isobutane	9.8	9.8	9.8	0.0	9.7	9.9	9.7	0.2
n-Butane	6.3	6.4	6.2	0.2	6.6	6.4	6.5	0.2
Isopentane	4.7	4.7	4.6	0.1	4.9	4.8	4.9	0.1
n-Pentane	2.0	1.9	2.0	0.1	1.8	1.8	1.8	0.0
		Av. = 0.18				0.44		

infrared method and 0.4 to 1.1% by mass spectrometer alone. The slight increase in average error of the components exclusive of butenes is not believed to be significant. All three synthetic mixtures show a positive error of approximately 1% on isobutene by the combination method. This is not believed to be characteristic of the method because, as shown in Table VII, values obtained on C_4 fractions check with those from infrared analysis even when the total butene concentration is as high as 90%.

The repeatability of the present method is shown in Table IX compared to that obtained with the mass spectrometer. The maximum spread is 0.4% by the mass spectrometer–infrared method as compared to 1.7% by the mass spectrometer alone. The average repeatability of all components is 0.18 and 0.44%, respectively.

CONCLUSION

The combination method may be applied to any mixture of light hydrocarbons where there is required a more accurate butene analysis than can be obtained by mass spectrometer alone. In process research and some refinery practice it is often necessary to obtain the best possible accuracy for these components. Previously it has been necessary to make low temperature distillations with a subsequent infrared analysis to obtain these data. The combined mass spectrometer–infrared method has been found to be fully adequate for all studies of this type encountered to date where the pentene and C_6 concentration is less than 3%.

This method easily may be applied to higher hydrocarbons of the gasoline range where the mass spectra of any two or more components may be similar. If these components exhibit sufficient difference in the infrared absorption spectrum, an accurate analysis by the combination method can be made. Because the basis of the method depends upon the distinguishing infrared spectra (or other properties) for those components of similar mass spectra in the particular type of mixture under examination, it may well fit into a number of schemes of analysis for "closed" systems of a finite number of components.

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Determination of Unsaturation of Butyl Rubbers and Certain Branched Olefins

Iodine Monochloride Method

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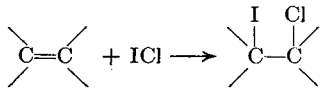
A RELIABLE and convenient method for the determination of unsaturation of hydrocarbon polymers and of olefins can generally be based on the addition of iodine monochloride to the carbon-to-carbon double bond. The reaction is represented as follows:



(1)

The procedure usually consists in adding an excess of iodine monochloride to the solution of unsaturated compound and, after a suitable reaction period, determining by titration the amount of iodine monochloride remaining. Although the iodine monochloride method yields accurate results for most olefins and polymers, it yields high results for certain olefins and polymers that are branched in the neighborhood of the double bond. A number of such compounds have been cited in the literature: 3-ethyl-2-pentene (*12*); trimethylethylene and limonene (*11*); isobutylene dimers, trimers, and tetramers (*3*); pinene, dipentene, and α-terpineol (*4*); dihydromyrcene and squalene (*1*); other branched olefins (*8*); and Butyl rubbers (*4, 12, 13*). Other examples are given herewith.

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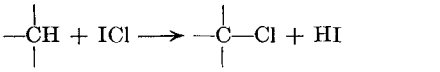
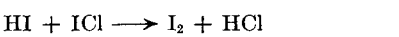
The reaction of iodine monochloride with highly branched olefins and polymers is abnormal in that the addition products formed possess steric strain and tend to decompose. The products of decomposition react further with iodine monochloride, generally leading to high results in the determination of unsaturation. Based upon the fact that the addition of iodine monochloride to the decomposition product is not so rapid as the addition of iodine monochloride to the original olefin or polymer, new procedures have been developed for the determination of unsaturation of highly branched ethylenic substances. The procedures have been shown to give reliable results for olefins such as the diisobutylenes and for copolymers, such as isoprene Butyl rubber and butadiene Butyl rubber.

In the reaction of iodine monochloride with highly branched olefins and polymers, large amounts of acid and iodine are formed in the reaction mixture, indicating the occurrence of side reactions. The high results in the determination of unsaturation and the formation of iodine and acid are often ascribed to substitution, although it has for some time been apparent that substitution cannot quantitatively account for the observed results.

Substitution may be represented as follows (*9*):



(2)



(3)

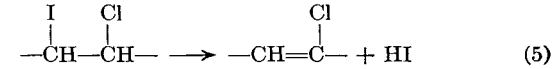
Reaction 2 indicates that one mole of halogen is reduced for each hydrogen atom of the olefin that is replaced. Reaction 3 has the effect of converting iodine monochloride to free iodine without affecting the total iodometric titer of the reaction mixture. Inasmuch as one molecule of acid is formed for every mole of halogen that is reduced by substitution, it would be expected that the experimental results in the determination of unsaturation could be corrected for substitution by application of the equation

$$a = b - c \qquad (4)$$

where a is the unsaturation (expressed as the number of moles of double bonds originally present), b is the decrease in the total iodometric titer (expressed as moles of halogen), and c is the number of moles of acid formed. [The value of c can be found by titrating the acid formed in the reaction mixture (*10*). Inasmuch as the molar amounts of acid and of iodine formed by substitution are equal (*9*), the value of c alternatively can be found by titrating the free iodine in the reaction mixture.]

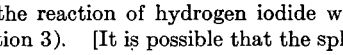
It has been observed, and is also evident from the data and discussion below, that Equation 4 yields a low value for the unsaturation of highly branched olefins and polymers (*1*, *6*), and, indeed, even for many polymers that are not highly branched (*9*). This means that the amount of acid (and of iodine) formed in the reaction of iodine monochloride with branched olefins and polymers is greater than can be accounted for by substitution.

Another side reaction, "splitting out," has been assumed to occur when halogens react with olefinic substances (*2*, *4*). It is thought that the halogen first adds to the double bond and that subsequently a molecule of hydrogen halide splits out. It seems especially probable that the splitting out reaction would occur when iodine monochloride is added to highly branched olefins and polymers, inasmuch as the addition products undoubtedly possess steric strain. Indeed, it was found impossible to construct steric models of the iodine monochloride addition products of certain branched olefins, owing to the large sizes of the halogen atoms and of alkyl groups. Those branched olefins which yield high results by the iodine monochloride method appear, from consideration of the models, to be unable to accommodate simultaneously an iodine and a chloride atom without considerable steric strain. Thus, it would seem reasonable that if these olefins add iodine monochloride momentarily, the resulting addition products would be unstable and would lose or split out hydrogen iodide or hydrogen chloride. On the basis of evidence given below it is concluded that only hydrogen iodide and no hydrogen chloride splits out. In general, the splitting out reaction is presumed to be represented as follows:



(5)

and is followed by the reaction of hydrogen iodide with iodine monochloride (Reaction 3). [It is possible that the splitting out of hydrogen iodide forms bonds of the type



as well as bonds of the type —CH=CCl—. The former bonds would be expected to react more rapidly with iodine monochloride than the latter. However, experimental evidence indicates that no highly reactive double bonds are formed as a result of splitting out.]

The double bond created by Reaction 5 would be expected to add iodine monochloride only slowly because of the retarding inductive effect of the chlorine atom. Indeed, it is known that the double bonds in polychloroprene (neoprene), which are of the type —CH=CCl—, add iodine monochloride only slowly (*6*, *7*).

As for the accuracy of the iodine monochloride method of determining unsaturation, the splitting out Reactions 5 and 3 would not affect the total iodometric titer and therefore would not directly affect the accuracy of the results. However, addition of iodine monochloride to the newly created double bonds would cause high results. In general, the greater the extent of splitting out, the higher the results due to this source of error.

The interpretation given above (splitting out and addition of iodine monochloride to the newly created double bonds) conforms with the results of a study of the reaction of iodine monochloride with a number of branched olefins and with Butyl rubbers. The interpretation also led to a modified iodine monochloride method which yields reliable results for highly branched olefins and polymers.

EXPERIMENTAL

Materials Used. Iodine monochloride stock solutions were prepared by dissolving Eastman practical grade iodine monochloride in analytical reagent grade carbon tetrachloride. The exact titers of the iodine monochloride solutions were determined by titration with thiosulfate solution. Small amounts of iodine trichloride, which sometimes occurs as an impurity in the Eastman iodine monochloride, do not interfere in the recommended procedures, described below. However, in the experiments in which free iodine is determined (experiments of Figures 1 to 3, 6, and 7), it is necessary to convert any iodine trichloride present in the stock solution to iodine monochloride by the addition of the proper amount of iodine. The amount of iodine trichloride originally present was determined by titration of a portion of the stock solution with iodide solution, as described elsewhere (*9*).

The olefins used were obtained, with one exception, from the National Bureau of Standards and were stated to be at least 99.9% pure. A sample of 3-methyl-2-pentene of unknown purity was also used.

Samples of unvulcanized Butyl rubber were kindly supplied by the Esso Laboratories, Standard Oil Development Company, Elizabeth, N. J. These samples were purified in the authors' laboratory as follows: Five grams of rubber were dissolved at room temperature in 500 ml. of *n*-hexane. The solution was filtered through glass wool to remove any suspended impurities and any gel that was present. The rubber was precipitated by adding the solution slowly to 2 liters of methanol. During the addition the methanol was stirred vigorously with a motor-driven stirrer.

The precipitated rubber was collected and dried for 24 hours at room temperature in a vacuum desiccator. The above procedure effectively removes the inhibitor (generally phenyl-2-naphthylamine) which is added to Butyl rubber to retard autoxidation.

Investigation of Reaction of Iodine Monochloride with Olefins and Polymers. Reaction mixtures were prepared as follows:

A carbon tetrachloride solution of the olefin was added to a volumetric flask, a solution of iodine monochloride in carbon tetrachloride was added, and the mixture was diluted to the mark with the same solvent. After varying reaction periods aliquot portions of the reaction mixture were removed and analyzed for total iodometric titer by titration with thiosulfate, amount of free iodine by titration with iodate in a hydrochloric acid medium, and amount of acid by the McIlhiney method (removal of the excess iodine monochloride and iodine with neutral aqueous iodide and thiosulfate solutions, followed by addition of iodate and titration of the liberated iodine with thiosulfate). The procedures for these determinations are described elsewhere (*9*). The amount of iodine monochloride remaining was found by subtracting the amount of free iodine from the total iodometric titer.

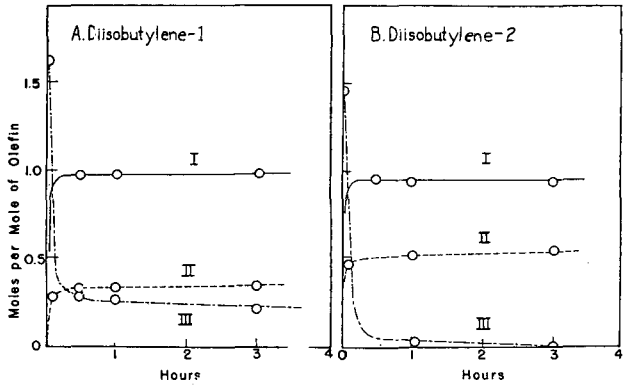


Figure 1. Reaction of Diisobutylenes with Iodine Monochloride

Initial molar ratio of ICl to olefin 1.5, initial concentration of olefin 0.02 *M*, temperature 25° C., solvent CCl_4
I. Decrease in total iodometric titer (expressed as moles of halogen)
II. Iodine formed
III. Iodine monochloride remaining

The results of the experiments are summarized in Figures 1 to 3, 6, and 7. The amounts of free iodine and of acid formed were corrected for the small amounts of these constituents present initially in the iodine monochloride stock solutions.

Recommended Procedure for Determination of Branched Olefins. A stock solution of olefin is prepared by adding a known weight of the sample to a volumetric flask and filling the flask to the mark with reagent grade carbon tetrachloride. If the sample is volatile, it should be weighed in a Victor Meyer bulb, and the bulb broken with a stirring rod under the surface of the carbon tetrachloride. Loss of olefin by volatilization may further be minimized by cooling the carbon tetrachloride to 0° before breaking the bulb. The concentration of olefin in the stock solution should be 0.01 to 0.03 *M* for best results. Twenty-milliliter portions of the olefin stock solution are added to a series of five to eight iodine flasks, each containing 40 ml. of carbon tetrachloride. Varying amounts of 0.05 *M* iodine monochloride solution in carbon tetrachloride are added to the flasks. For convenience the iodine monochloride solution may be dispensed from a buret (no stopcock grease!). The amounts of iodine monochloride used should be such as to provide an initial molar ratio of halogen to olefin of about 0.5 to 3 (see Figures 4, 5, 8, and 9). The iodine flasks are then stoppered and allowed to stand at room temperature for 1 hour, 40 ml. of 0.5 *M* aqueous acetic acid solution and 1 gram of potassium iodide are added, the mixture is shaken, and the liberated iodine is titrated with standard 0.05 or 0.1 *M* thiosulfate solution. Starch solution is added when the end point is approached.

In order to find the titer of the iodine monochloride, a blank reaction mixture containing no olefin is prepared and titrated in the same way as the sample reaction mixtures. Only one blank need be prepared for each series of sample reaction mixtures.

The total iodometric titer of each reaction mixture is found from the equation

$$\text{Millimoles of halogen} = \frac{\text{ml. of thiosulfate} \times \text{normality of thiosulfate}}{2} \quad (6)$$

The decrease in total iodometric titer, expressed in millimoles of halogen per gram of sample and represented by d, for each reaction mixture is given by the expression

$$d = \frac{(\text{millimoles of ICl added}) - (\text{millimoles of halogen remaining})}{\text{weight of sample in 20 ml. of stock solution}} \quad (7)$$

The calculated values of d are plotted against the initial ratio of halogen to olefin (expressed in any convenient units). An illustration of this plot is given in Figures 4 and 5. The value of d corresponding to the discontinuity in the curve is designated as d_d and is equal to the unsaturation of the sample (expressed as millimoles of double bonds per gram of sample).

If it is desired to express the unsaturation of the sample as iodine number (I.N.), the following relation can be used:

$$\text{I.N.} = d_d \times 25.38 \quad (8)$$

If it is desired to express the unsaturation of the sample as percentage of theoretical, the equation is:

$$\%\ \text{of theoretical} = d_d \times \frac{\text{M.W.}}{10} \quad (9)$$

where M.W. is the molecular weight of the olefin.

Recommended Procedure for Determination of Unsaturation of Butyl Rubbers. The Butyl rubber is purified as described above. A stock solution is prepared by dissolving a weighed portion of the rubber in carbon tetrachloride at room temperature. The size of the sample should be chosen to yield a solution that is 0.005 to 0.02 *M* in double bonds—i.e., in isoprene or butadiene units. The dissolution of the sample requires from several hours to a day, but may be hastened by putting the flask in a mechanical shaker. (For other rapid methods of dissolving the sample, see *7* and *4*.)

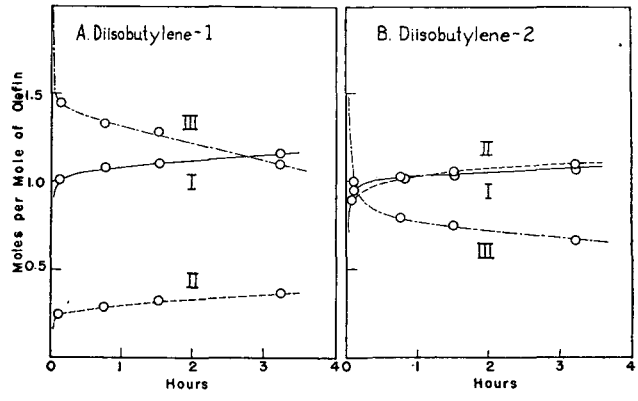


Figure 2. Reaction of Diisobutylenes with Iodine Monochloride

Same conditions as in Figure 1 except initial molar ratio of ICl to olefin 3.0

Twenty-milliliter portions of the stock solution are added to a series of five to eight iodine flasks, each containing 20 ml. of carbon tetrachloride. (If the unsaturation of the Butyl rubber is low, 50- instead of 20-ml. portions of the stock solution may be used. In this case the concentration of double bonds in the stock solution may be as low as 0.002 *M*. No additional carbon tetrachloride should be added.) Varying amounts of 0.02 *M* iodine monochloride are added to the flasks. For best results the amounts of iodine monochloride added should correspond to initial molar ratios of halogen to double bonds varying between 0 and 3. The reaction mixtures are allowed to stand 1 hour in the glass-stoppered flasks and then the iodometric titer is determined as described above. The decrease in total iodometric titer is calculated for each reaction mixture from Equation 6. The value of d is plotted against the initial ratio of iodine monochloride to olefin (expressed as millimoles of halogen per gram of sample).

This plot is illustrated in Figures 8 and 10. The value of d corresponding to the discontinuity in the curve (d_d) is equal to the unsaturation of the polymer expressed in millimoles of double bonds per gram. The relation between d_d and the mole per cent of copolymerized isoprene or butadiene is

$$\text{Mole \% isoprene or butadiene} = d_d \times 5.61 \qquad (10)$$

Equation 10 is not exact, but is based on the assumption that the average molecular weight of the monomer units in Butyl rubbers is 56.1, the molecular weight of isobutylene itself (*4*). Equation 10 is sufficiently accurate for all practical work, provided that the Butyl rubber does not contain more than 5% isoprene or 10% butadiene (see below). The relation between d_d and the iodine number of the rubber is given in Equation 8.

REACTION OF IODINE MONOCHLORIDE WITH DIISOBUTYLENES

2,4,4-Trimethyl-1-pentene(diisobutylene-1) and 2,4,4-trimethyl-2-pentene(diisobutylene-2) were chosen as representative highly branched olefins. The experimental results of the reaction of iodine monochloride with these two olefins are shown in Figures 1 to 3. In the experiments of Figure 1 the initial molar ratio of iodine monochloride to olefin is 1.5 It is seen that the decrease in total iodometric titer is 1.0 mole of halogen per mole of olefin, the theoretical decrease expected for addition of iodine monochloride to an olefin. However, large amounts of iodine are formed in the reaction mixtures. The source of this iodine is not substitution, for substitution would be accompanied by a corresponding decrease in iodometric titer. Furthermore, when iodine monochloride was allowed to react with 2,4,4-trimethylpentane (hydrogenated diisobutylene) under the conditions of Figure 1, the decrease in iodometric titer was less than 0.01 mole of halogen per mole of hydrocarbon after a 4-hour reaction period—the substitution was practically negligible. It can be concluded that under the experimental conditions of Figure 1 the addition of iodine monochloride to the diisobutylenes is very rapid and that splitting out is also rapid. It can be seen from Figure 1 that the concentration of iodine monochloride in the reaction mixture after the initial stages of reaction was very small. Consequently, no addition to the newly created double bonds occurred. It is for this reason that the theoretical decrease in iodometric titer was found.

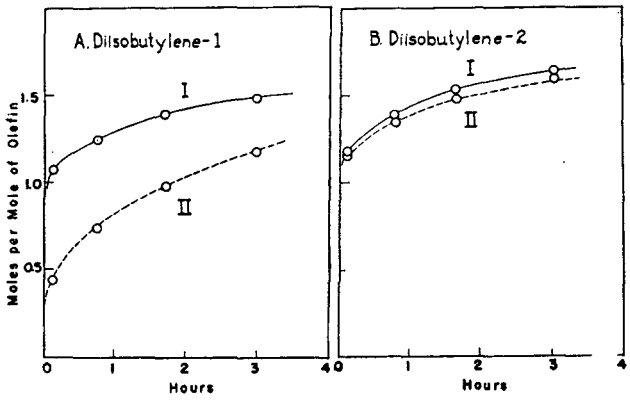


Figure 3. Reaction of Diisobutylenes with Iodine Monochloride

Same conditions as in Figure 1 except initial molar ratio ICl to olefin 5.0

In the experiments of Figure 2 the initial ratio of iodine monochloride to olefin was 3.0. The decrease in total iodometric titer was about 1 mole of halogen per mole of olefin in the initial stages of reaction (0 to 0.5 hour). The total iodometric titer decreased slowly over longer reaction periods, indicating that slow addition to the newly created double bonds was taking place. The molar amount of iodine formed in the reaction of iodine monochloride with 2,4,4-trimethyl-2-pentene was equal to the molar decrease in iodometric titer; this indicated that the splitting out of hydriodic acid from the addition product is quantitative and also that the product formed by the addition of iodine monochloride to the newly created double bonds quantitatively splits out hydriodic acid. The splitting out of hydrogen iodide from the secondary addition product ($C_8H_{15}ICl_2$) would be expected from a consideration of the steric models.

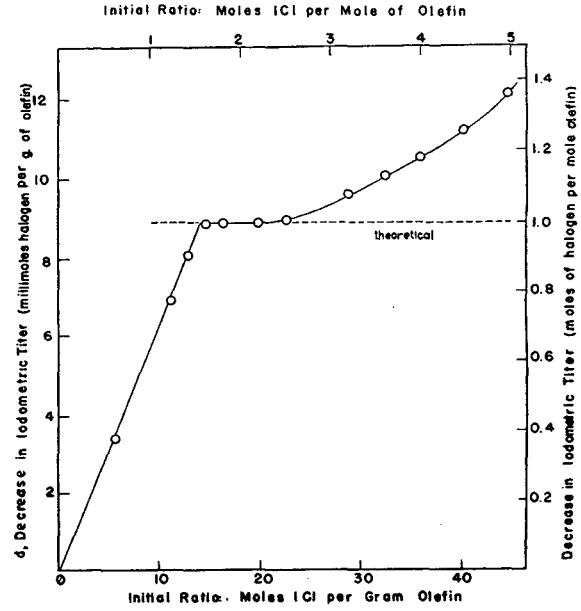


Figure 4. Determination of 2,4,4-Trimethyl-2-pentene by Recommended Procedure

In the experiments of Figure 3 the initial ratio of iodine monochloride to olefin was 5.0. The results are similar to the experiments of Figure 2 except that, as would be expected, the addition of iodine monochloride to the newly created double bonds is more pronounced. In the experiments of Figure 3 the apparent, uncorrected unsaturation after a reaction period of 3 hours was 150% for 2,4,4-trimethyl-1-pentene and 160% for 2,4,4-trimethyl-2-pentene (theoretical value for both olefins is 100%). If the iodine formed in these reactions is assumed to be due to substitution (Reactions 2 and 3) the "corrected" unsaturation found from Equation 4 is 30% for 2,4,4-trimethyl-1-pentene and 5% for 2,4,4-trimethyl-2-pentene instead of the theoretical value 100%.

From a consideration of steric models (Fisher-Hirschfelder-Taylor models) it is expected that one of the isomers of the addition product of 2,4,4-trimethyl-1-pentene—namely, 1-iodo-2-chloro-2,4,4-trimethylpentane—does not possess steric strain. The other isomer of this addition product—namely, 1-chloro-2-iodo-2,4,4-trimethylpentane—would be expected to be under great steric strain. In contrast to this, both isomers of the addition product of 2,4,4-trimethyl-2-pentene would be expected to possess steric strain. This accounts for the fact that splitting out occurs only partially in the case of 2,4,4-trimethyl-1-pentene but completely in the case of 2,4,4-trimethyl-2-pentene. (In regard to the addition products of 2,4,4-trimethyl-2-pentene, it is interesting to note that if 2-chloro-3-iodo-2,4,4-trimethylpentane is formed momentarily, it would be expected to decompose into iodine monochloride and 2,4,4-trimethyl-2-pentene again. This expectation is based on the assumption of steric strain and on the fact that this addition product cannot lose hydrogen iodide, because neither the number 2 nor the number 4 carbon atom possesses the hydrogen atom required for the formation of hydrogen iodide.)

In summary of the above discussion the reaction of iodine monochloride with diisobutylenes is the result of a number of individual reaction steps:

$$C_8H_{16} + ICl \longrightarrow C_8H_{16}ICl \quad \text{Very fast} \quad (11)$$

$$C_8H_{16}ICl \longrightarrow C_8H_{15}Cl + HI \quad \text{Fast} \quad (12)$$

$$HI + ICl \longrightarrow I_2 + HCl \quad \text{Very fast} \quad (13)$$

$$C_8H_{15}Cl + ICl \longrightarrow C_8H_{15}ICl_2 \quad \text{Slow} \quad (14)$$

$$C_8H_{15}ICl_2 \longrightarrow C_8H_{14}Cl_2 + HI \quad \text{Fast} \quad (15)$$

$$HI + ICl \longrightarrow I_2 + HCl \quad \text{Very fast} \quad (16)$$

Reaction 11 represents rapid addition, Reaction 12 represents rapid splitting out of hydrogen iodide, Reaction 14 represents slow addition of iodine monochloride to newly created double bonds, and Reaction 15 represents splitting out of hydrogen iodide from the secondary addition product.

It was found, by determination of the acid in a number of the reaction mixtures, that the molar amount of iodine formed was in all cases substantially equal to the molar amount of acid formed. This result would be expected on the basis of the above scheme.

Consideration of Reactions 11 to 14 leads to the expectation that reliable results may be obtained in the determination of unsaturation of branched olefins if the appropriate excess of iodine monochloride over olefin is used. Thus, if the initial excess of iodine monochloride is small and if Reaction 12 is much faster than Reaction 14 but not nearly so fast as Reaction 11, the decrease in iodometric titer should be equivalent to the amount of olefin initially present. Under these conditions Reaction 11 goes to completion and Reactions 12 and 13 convert the excess iodine monochloride into free iodine, which does not react further.

In Figure 4 are shown the results of experiments in which the initial ratio of iodine monochloride to 2,4,4-trimethyl-2-pentene was varied from 0.6 to 5. The following conclusions are drawn from Figure 4.

If the initial molar ratio of halogen to olefin is less than 1.5, the decrease in total iodometric titer is less than theoretical. This indicates that the rate of Reaction 12 is less than but comparable to that of Reaction 11. Thus, if the ratio is less than 1.5, Reaction 11 and Reactions 12 and 13 compete for iodine monochloride. This explains why the iodine monochloride method sometimes yields low results in the determination of branched olefins (*4*).

If the initial molar ratio of halogen to olefin is between 1.5 and 2.5, the theoretical decrease in iodometric titer is obtained. This is reasonable on the basis of the discussion given above.

If the ratio is greater than about 2.5, the decrease in iodometric titer is larger than theoretical, due to Reaction 14.

When both the iodine monochloride and the 2,4,4-trimethyl-2-pentene were diluted without changing the ratio of the two reactants, the relative importance of Reaction 14 as compared with Reaction 12 was diminished. This is to be expected, because Reaction 12 is presumably a first-order reaction while Reaction 14 is of higher order. As a result of this effect, values of unsaturation close to the theoretical value can be obtained when the reaction mixture is very dilute, even if the initial ratio of iodine monochloride to olefin is 4 or more. In general, it is not advisable, however, to carry out the determination of unsaturation at high dilution because of the difficulty in titrating very dilute solutions.

Experiments similar to those of Figure 4 were carried out in which 2,4,4-trimethyl-1-pentene was used instead of 2,4,4-trimethyl-2-pentene (Figure 5). It is seen that the theoretical decrease in iodometric titer is obtained only if the initial ratio of halogen is within certain narrow limits. This would be expected from the fact that the splitting out Reaction 12 is far from complete in the case of 2,4,4-trimethyl-1-pentene (whereas it is complete in the case of 2,4,4-trimethyl-2-pentene). Consequently, in the reaction of iodine monochloride with 2,4,4-trimethyl-1-pentene, the excess of iodine monochloride is not converted into free iodine even when the excess of iodine monochloride is small. On the other hand, Reaction 14 undoubtedly is not so rapid in the case of 2,4,4-trimethyl-1-pentene as in the case of 2,4,4-trimethyl-2-pentene. Consequently, if the initial ratio of halogen to olefin is high—e.g., 4 or 5—the decrease in total iodometric titer is not so large in the reaction of 2,4,4-trimethyl-1-pentene as in the reaction of 2,4,4-trimethyl-2-pentene.

As can be seen from Figures 4 and 5, a method for the determination of the diisobutylenes and similar branched olefins is the following: A number of reaction mixtures are prepared with varying ratios of iodine monochloride to olefin. After a suitable reaction period the decrease in iodometric titer of each reaction mixture is determined and the results are plotted as shown in Figures 4 and 5. The discontinuity in the curve corresponds to the unsaturation of the sample (see recommended procedure).

The procedure should also be applicable to a mixture of branched and unbranched olefins, as well as to the determination of terpenes (*5*, *11*).

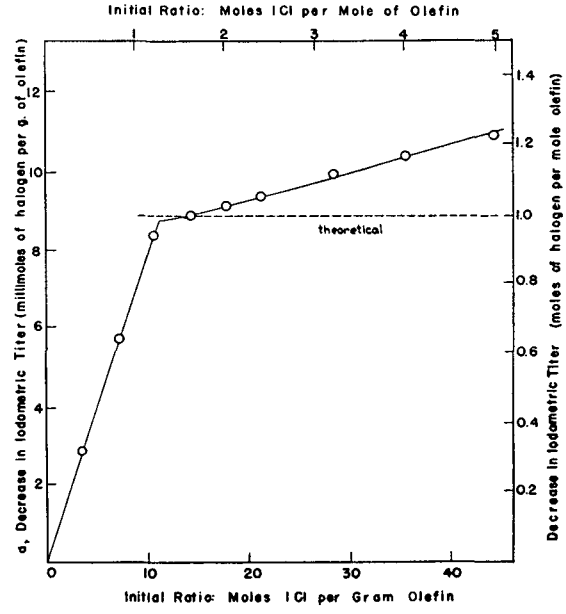


Figure 5. Determination of 2,4,4-Trimethyl-1-pentene by Recommended Procedure

The results given in Figures 1 to 5 show that iodine monochloride first adds to the double bonds and that subsequently hydrogen iodide splits out from the addition product. The direct reaction

$$\begin{matrix} H & H \\ | & | \\ -C=C- \end{matrix} + ICl \longrightarrow \begin{matrix} H & Cl \\ | & | \\ -C=C- \end{matrix} + HI \quad (17)$$

apparently does not occur. Reaction 17 is eliminated by the following reasoning: Inasmuch as the reaction of hydrogen iodide with iodine monochloride is very rapid (presumably much more rapid than Reaction 17) we can write, in place of Reaction 17,

$$\begin{matrix} H & H \\ | & | \\ -C=C- \end{matrix} + 2ICl \longrightarrow \begin{matrix} H & Cl \\ | & | \\ -C=C- \end{matrix} + I_2 + HCl \quad (18)$$

In the case of a substance like 2,4,4-trimethyl-2-pentene, the addition product of which is completely unstable (see Figures 2,*B*, and 3,*B*), it would be expected from Equation 18 that if the initial ratio of iodine monochloride to double bonds was 1.5, the decrease in total iodometric titer would be only 1.5/2 or 0.75 mole of halogen per mole of double bonds. Actually, it was found (Figure 1,*B*) that the decrease in iodometric titer was 1.0

Table I. Reaction of Iodine Monochloride with Olefins and Polymers

(Initial molar ratio of halogen to olefin 1.5, initial concentration of double bonds 0.02 *M*, solvent CCl_4, temp. 25° C.)

Expt.	Olefin or Polymer	Structure	Apparent Unsaturation, %	Iodine Formed, Moles per Mole of Double Bonds × 100: In first 0.1 hour	In next hour
1	Unbranched olefins (1-octene, 1-pentene, *cis*-2-pentene, *trans*-2-pentene)	RCH=CHR and RCH=CH_2	98–100	0–1	0–1
2	3,3-Dimethyl-1-butene	$CH_2=CH-\overset{CH_3}{\overset{\vert}{C}}-CH_3$ (CH_3)	98	0	0.2
3	2-Methyl-2-butene	$CH_3-\overset{CH_3}{\overset{\vert}{C}}=CH-CH_3$	...	0	0
4	3-Methyl-1-butene	$CH_2=CH-\overset{CH_3}{\overset{\vert}{C}}H-CH_3$	101	2.7	0
5	3-Methyl-2-pentene[a]	$CH_3-\overset{CH_3}{\overset{\vert}{C}}H=C-CH_2-CH_3$	98	5.5	6
6	2-Methyl-1-butene	$CH_2=\overset{CH_3}{\overset{\vert}{C}}-CH_2-CH_3$	106	7.7	2
7	2,4,4-Trimethyl-1-pentene	$CH_2=C(CH_3)-CH_2-\overset{CH_3}{\overset{\vert}{C}}(CH_3)-CH_3$	108[b]	25[b]	4[b]
8	2,4,4-Trimethyl-2-pentene	$CH_3-\overset{CH_3}{\overset{\vert}{C}}=CH-\overset{CH_3}{\overset{\vert}{C}}(CH_3)-CH_3$	103[b]	90[b]	13[b]
9	Isoprene Butyl rubber	.....	...	29–42[b]	...
10	Butadiene Butyl rubber	.....	...	8–11[b]	...

[a] Purity of sample of 3-methyl-2-pentene unknown.
[b] Initial molar ratio of iodine monochloride to double bonds 3.0.

REACTION OF IODINE MONOCHLORIDE WITH OTHER BRANCHED OLEFINS

In order to find which olefin structures cause splitting out, several branched olefins were allowed to react with iodine monochloride, and the amounts of free iodine formed after 0.1- and 1-hour reaction periods were determined. The results are given in Table I. The amount of splitting out is represented approximately by the amount of iodine formed in the first 0.1 hour (*9*), although splitting out may not be rapid in all cases. Moreover, slow addition of iodine monochloride to newly created double bonds may occur, resulting in further splitting out over an extended period of time. Addition to newly created double bonds causes the "apparent unsaturation" to be higher than theoretical. In Table I the "apparent unsaturation" is the uncorrected percentage of theoretical unsaturation found after a reaction period of 1 hour.

From Table I it is seen that no detectable splitting out occurs in the reaction of iodine monochloride with olefins that do not possess side alkyl groups. The extent of splitting out is also small for straight-chain olefins possessing only one side methyl group. Construction of steric models indicates that the addition products of these two types of olefins are not under steric strain. However, if additional alkyl groups are added to the α or β carbon atoms, steric strain usually results. The steric strain is reflected in the experimental data of experiments 7 to 10.

It can be concluded from Table I that the ordinary iodine monochloride method is reliable for determination of unbranched olefins or for branched olefins of the type used in experiments 2 to 5. It is not applicable for the more highly branched olefins or polymers of experiments 7 to 10.

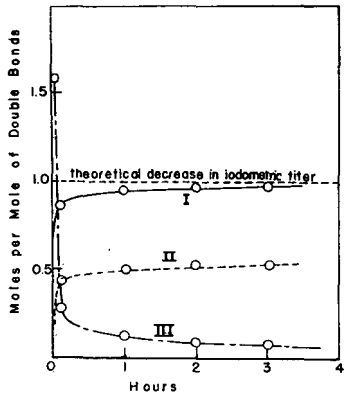


Figure 6. Reaction of Isoprene Butyl Rubber with Iodine Monochloride

Initial molar ratio of ICl to double bonds 1.5, initial concentration of polymer 5.61 grams per liter, initial concentration of ICl 0.00314 *M*. I, II, and III as in Figure 1

REACTION OF IODINE MONOCHLORIDE WITH BUTYL RUBBERS

Butyl rubbers are copolymers of isobutylene and either isoprene or butadiene. The amount of isoprene or butadiene in the copolymer is small, generally about 0.2 to 5 mole % of the monomer units. The unsaturation possessed by Butyl rubbers is presumably due entirely to the isoprene or butadiene units and consequently a method for determination of unsaturation provides a means for determining these constituents.

Inasmuch as the structure of the isobutylene-isoprene copolymer (isoprene Butyl rubber) closely resembles that of the diisobutylenes, a large amount of splitting out would also be expected to occur in the reaction of iodine monochloride with isoprene Butyl rubber. Figures 6 and 7, which show the reaction of iodine monochloride with isoprene Butyl rubber, should be compared with

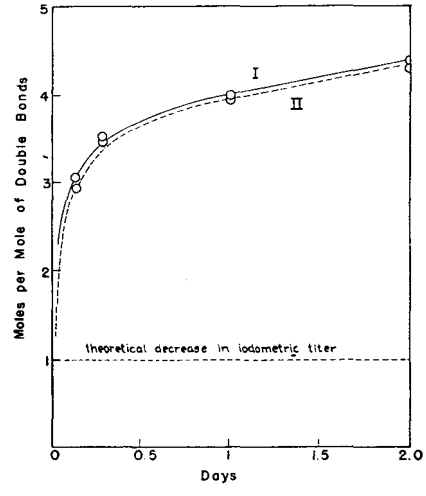


Figure 7. Reaction of Isoprene Butyl Rubber with Iodine Monochloride

Initial molar ratio of ICl to double bonds 11.0, initial concentration of polymer 2.46 grams per liter, initial concentration of ICl 0.025 *M*. I and II as in Figure 1

Figures 1,*B*, and 3,*B*, respectively. It is seen that isoprene Butyl rubber and 2,4,4-trimethyl-2-pentene do indeed react in a very similar manner. The theoretical decrease in iodometric titer found in the experiment of Figure 6 indicates that the source of iodine is splitting out, not substitution. In further support of this supposition, very little free iodine is formed in the reaction of iodine monochloride with polyisobutylene that contains no copolymerized butadiene or isoprene. Thus, in an experiment similar to that of Figure 6 less than one tenth as much iodine was formed when pure polyisobutylene was substi-

tuted for the isobutylene-isoprene copolymer (equal weights of polymer used in each experiment, reaction period 1 hour).

In Figure 8 are shown the results of the determination of unsaturation of isoprene Butyl rubber by the recommended procedure. The unsaturation found, 4.6 mole % isoprene, is very close to the "theoretical" value, 4.7 obtained by the perbenzoic acid method. The latter method is known to be reliable for this type of polymer and will be described in a subsequent publication. The value found from Figure 8 is also close to the value 4.9 found for the same sample at the Esso Laboratories by the iodine–mercuric acetate method (*4*).

The reaction of butadiene Butyl rubber with iodine monochloride would not be expected to be accompanied by an exceptionally large amount of splitting out, inasmuch as the butadiene units in the copolymer do not contain side alkyl groups. Some splitting out can be expected, however, because of the proximity of the butadiene units to the highly branched isobutylene units.

In Figure 9 is shown the reaction of iodine monochloride with butadiene Butyl rubber. The conditions of this experiment are essentially the same as in the corresponding experiment with isoprene Butyl rubber (Figure 6). Comparison of Figures 6 and 9 shows that the amount of splitting out which occurs in the reaction of the butadiene copolymer is relatively small. From Figure 9 it can also be seen that the decrease in iodometric titer is nearly theoretical, even though a relatively large excess of iodine monochloride is present throughout the reaction period.

In Figure 10 are shown the results of the determination of unsaturation of butadiene Butyl rubber by the recommended procedure. An unsaturation of 6.0 mole % is found as compared with the "theoretical value" 6.3. The latter value was found by the iodine–mercuric chloride method, which is applicable to butadiene Butyl rubber (to be described in a subsequent publication). The unsaturation of the same sample was found to be 4.1 mole % at the Esso Laboratories by the iodine–mercuric acetate method. However, the Esso value was calculated using an empirical factor of 1.5 molecules of iodine per double bond (*4*), instead of the theoretical factor 1.0. According to the authors' study of the iodine–mercuric acetate method, the theoretical factor 1.0 should be used for olefins and polymers that are not branched in the immediate neighborhood of the double bond. A recalculation of the Esso value, using the factor 1.0, yields a value of unsaturation of 6.2 in good agreement with the results given above.

As would be expected, and as can be seen from Figure 10, the effect of excess iodine monochloride on apparent unsaturation is much less in the case of butadiene Butyl rubber than in the case of isoprene Butyl rubber. Indeed, a reasonably accurate value of unsaturation of the butadiene Butyl rubber can be found from a single determination of the decrease in total iodometric titer, provided that the initial ratio of iodine monochloride to double bonds is between 2 and 5 and the reaction period is 1 hour at room temperature.

The recommended procedures described above for determination of unsaturation of highly branched olefins and polymers are not adaptable to routine analyses because they are not rapid. Nevertheless, the procedures are of value in the research laboratory and in the standardization of empirical, routine procedures. A very convenient procedure for determination of unsaturation of isoprene Butyl rubbers is the iodine–mercuric acetate method described by Gallo, Wiese, and Nelson (*4*). This method is of much practical importance, although the interpretation of the experimental results involves a numerical factor which at present must be considered empirical.

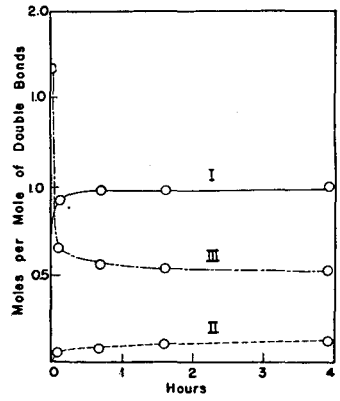


Figure 9. Reaction of Butadiene Butyl Rubber with Iodine Monochloride

Conditions similar to those of Figure 6. I, II, and III as in Figure 1

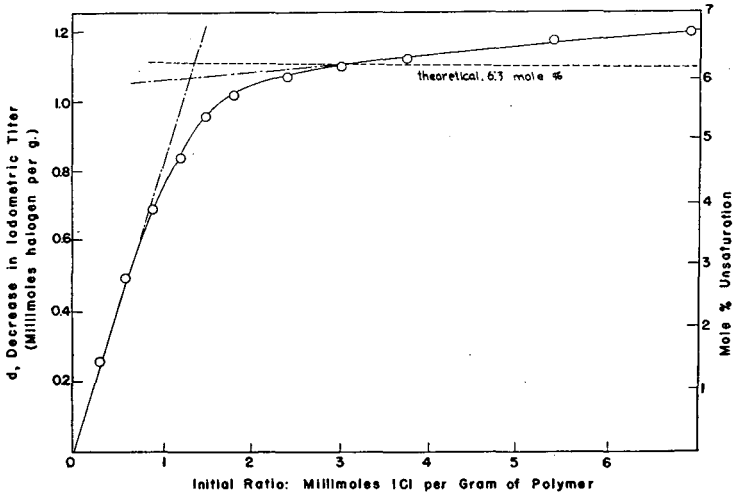


Figure 10. Determination of Unsaturation of Butadiene Butyl Rubber by Recommended Procedure

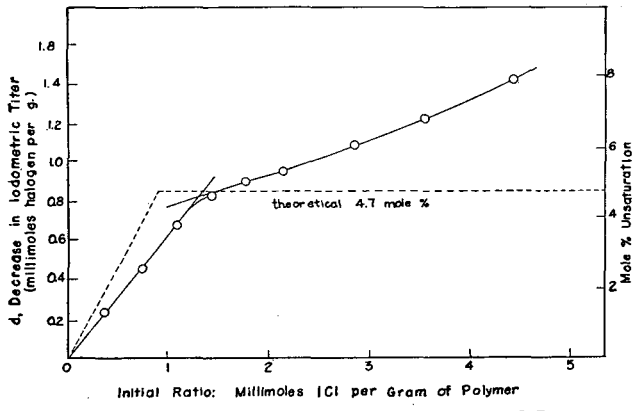


Figure 8. Determination of Unsaturation of Isoprene Butyl Rubber by Recommended Procedure

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Determination of Free Carbon in Cured Rubber Stocks

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A method for the determination of free carbon in vulcanized rubber stocks is described. The sample is softened in boiling *p*-dichlorobenzene before treatment with *tert*-butylhydroperoxide in the presence of osmium tetroxide. No difficulties are encountered in the filtration of the carbon black. The carbon black is washed on the filter with dilute nitric acid to remove acid-soluble inorganic fillers. The method has been successfully applied to natural rubber, GR-S, Butyl rubber, and neoprene. No correction is necessary.

IN THE course of current studies on the interaction of rubber and carbon black, a method for the determination of the free carbon content of vulcanized rubber stocks, which is simple, rapid, and of an accuracy sufficient for control purposes, was developed.

The procedures which have been used for the control of rubber–carbon black batches may be classified in three groups. Widest adoption has been gained by the methods involving the degradation of the rubber matrix and most compounding ingredients by hot concentrated nitric acid. Typical of these is the current A.S.T.M. method (*1*). Butyl rubber (GR-I) and neoprene, which are resistant to nitric acid decomposition, cannot be analyzed in this way. McCready and Thompson (*8*) have suggested preliminary digestion of the sample in hot mineral seal oil to make the method applicable for Butyl rubber. The chief disadvantage of the nitric acid procedures is the difficulty experienced in filtration of the carbon, because the finely divided particles tend to run through the asbestos filter. Because some of the decomposition products of the rubber are retained by the carbon, the results are high and variable; an empirical correction of 0.95 must be applied. A recent modification by Louth (*7*) eliminates many of these disadvantages, but adds a few of its own. The procedure involves preliminary softening of the sample in boiling 1,1,2,2-tetrachloroethane (which permits analysis of Butyl rubbers and neoprene), the use of ether to coagulate the carbon during the filtration, and drying of the carbon at 250° instead of 110° C. to avoid application of the correction factor. The unpleasant nature of 1,1,2,2-tetrachloroethane and the possibility of violent reaction between the nitric acid and ether in the filtration step in spite of all precautions constitute the disadvantages of this procedure.

The extraction of the rubber by a high boiling inert solvent has been little used, partly because of the length of time required (*2*, *5*).

The third group of methods involves dry distillation of rubber from the carbon black and inorganic fillers in an inert atmosphere and subsequent burning of the carbon black in oxygen. The method was first used for natural rubber by Decker (*4*) and modified for the analysis of GR-S by the National Bureau of Standards (*9*). Bauminger and Poulton suggest collecting and weighing the carbon dioxide evolved in addition to the usual determination of the weight loss during the combustion (*3*). These methods are rapid if two combustion furnaces are available. However, standard sample blanks must be run with each set of samples to correct a slight empirical error in the method. In addition, inorganic fillers which change weight during the two combustions may prove troublesome.

The method here proposed makes use of the fact that rubber containing ethylenic double bonds is oxidatively cleaved by *tert*-butylhydroperoxide in the presence of osmium tetroxide. The resulting fragments are compounds of small molecular weight. The reaction has previously been used for the determination of polystyrene in GR-S (*6*). The applicability of the method was tested by the analysis of natural rubber, GR-S, Butyl rubber, and neoprene, and found successful in each case.

OUTLINE OF METHOD

The sample is softened in gently boiling *p*-dichlorobenzene, and then treated with *tert*-butylhydroperoxide in the presence of a catalytic quantity of osmium tetroxide. The mixture is filtered through a Gooch crucible. The carbon on the filter is washed with benzene, and then with dilute nitric acid and water to dissolve inorganic fillers. The filter is dried at 350° C., cooled, and weighed. The carbon is burned off at low red heat, and the crucible is cooled and reweighed. The loss in weight represents the amount of carbon originally present.

REAGENTS

tert-Butylhydroperoxide, commercial grade (minimum 60% *tert*-butylhydroperoxide), is obtained from the Lucidol Division, Novadel-Agene Corporation, Buffalo, N. Y. The reagent is stable for several months if kept in a cool place.

Osmium tetroxide is prepared by dissolving 0.08 gram in 100 ml. of reagent grade benzene. The solution should be protected from light and discarded at the first appearance of a black precipitate.

p-Dichlorobenzene, commercial, Paradow.

Nitric acid, C.P.

Gooch crucibles are used for filtration. The asbestos pad consists of a layer of medium fibers covered by a layer of fine fibers. It is ignited at 800° C. for at least an hour.

PROCEDURE

Cut the rubber into small cubes and weigh out samples of 0.2 to 0.25 gram accurately. Place 20 grams of *p*-dichlorobenzene in a 125-ml. Erlenmeyer flask with ground-glass joint, fitted with a reflux condenser, or in a 150-ml. beaker, which may be covered by a 125-ml. Erlenmeyer flask filled with cold water. Heat on the hot plate until the *p*-dichlorobenzene is melted, add the rubber sample, and adjust the temperature of the hot plate so that the liquid boils gently. Softening for half an hour is sufficient in most cases. Cool the solution slightly (80° to 90° C.), and add 5 ml. of *tert*-butylhydroperoxide and 1 ml. of osmium tetroxide solution. Heat to about 120° C. and keep there for 30 minutes. Cool the mixture to 50° to 60° C. and add 25 ml. of reagent grade benzene. Filter through the Gooch crucible while still slightly warm. No difficulty is encountered in filtration; the carbon settles out readily and has no tendency to run through the filter. (In isolated cases, the addition of a few milliliters of ether may serve to speed the filtration.) Wash the filter and beaker with benzene; empty the filter flask, and wash the filter with two 5-ml. portions of warm 1 to 2 nitric acid, using gentle suction. Wash with several portions of distilled water, dry the crucible at 325° to 350° C. for 0.5 hour, cool in a desiccator, and weigh quickly. Ignite at 750° to 800° C. cool, and weigh. The loss in weight represents the carbon present in the original sample.

Calculate the per cent of free carbon from the expression:

$$\% \text{ free carbon} = \frac{\text{wt. of crucible and carbon} - \text{wt. of crucible after ignition}}{\text{wt. of sample}} \times 100$$

ANALYTICAL RESULTS

Four samples of carbon black, corresponding in weight to 25 to 30% carbon black loadings of rubber samples 0.2 to 0.25

Table I. Blank Analyses of Carbon Black

Carbon Black	Weight Taken, Gram	Weight Found, Gram
No rubber present		
Philblack O (RF)	0.0390	0.0379
Sterling 99 (FF)	0.0622	0.0607
Ca. 0.14 gram of GR-S present		
Spheron 6 (MPC)	0.0514	0.0501
Philblack A (HMF)	0.0752	0.0746

Table II. Analyses of Vulcanized Rubber Stocks

Type of Rubber	Inorganic Filler	Amt. of Filler, %	Nominal Carbon Black, %	No. of Detns.	Carbon Found, % (Av.)	Av. Deviation of Mean, % Abs.
Natural	Zinc oxide	2	30.4	7	30.5	0.21
Neoprene	Magnesium oxide	2.6	23.6	5	23.9	0.21
Type GN	Zinc oxide	3.8				
Butyl	Zinc oxide	3.1	28.8	3	28.6	0.13
GR-S	Zinc oxide	1.9	28.2	5	28.3	0.20

gram in weight, were run through the entire procedure. To two of the samples, sufficient GR-S was added to make the combined weight approximately 0.2 gram. It appears from the results given in Table I that no correction factor is necessary.

Four specimens of cured rubber stock were analyzed by this procedure. The authors are indebted to G. D. Louth of Firestone Tire and Rubber Company, who furnished the certified stock with information on the kind and amount of inorganic filler. The results of the analyses are given in Table II.

The average deviation of a single determination never exceeded 0.6% absolute. The method appears sufficiently accurate to recommend it for control work on rubber–carbon black master batches.

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Comparison of Calcium 45 Oxalate and Carbonate Precipitates for Radioactive Assays

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Oxalate and carbonate methods have been compared with respect to preparation of suitable precipitates for radioactivity assays of calcium 45. Interference of magnesium, phosphorus, and aluminum was studied in regard to weight of precipitate and influence on activity measurements. Because of the common presence of inerfering ions, the oxalate method is indicated to be more satisfactory than the carbonate procedure for the preparation of calcium precipitates for radioactivity assays, especially in biological materials.

CALCIUM is customarily precipitated from a solution of the ash of biological materials as the oxalate (*1*) and in this form it is generally collected by filtration for radioactive assay of calcium 45 (*3, 4, 6*). In this investigation the oxalate method was compared with a carbonate procedure for the preparation of suitable calcium precipitates that might be used for routine analysis of radioactive calcium 45 in biological materials.

EXPERIMENTAL

The oxalate procedure (*1*) requires heating approximately 50 ml. of a solution of the sample to boiling temperature, adding 10 ml. of saturated ammonium oxalate, and then adjusting the pH to the intermediate color of methyl red indicator (approximately pH 4.8). In making wet digestions of biological materials with concentrated nitric acid preparatory to calcium 45 determinations, it appeared that a more simple procedure would be to neutralize an aliquot of the digest with sodium hydroxide, add sodium carbonate, stir, let stand a few hours, and then filter the carbonate precipitate. To evaluate this procedure, precipitates of solutions of known calcium content and samples of biological material were prepared by the oxalate and carbonate procedures. The precipitates were collected on Whatman No. 42 filter paper by means of a suitable funnel, ring, and disk assembly, such as that supplied by Tracerlab, Inc. (*7*). This equipment provides a very reproducible means for preparing precipitates for radioactive assay. The surface area of all precipitates was 2.835 sq. cm. Thin mica-window (1.5 to 2.0 mg. per sq. cm.) Geiger-Müeller tubes were used in conjunction with commercial scalers for the activity measurements.

RESULTS AND DISCUSSION

In Figure 1, self-absorption curves show the rate at which the calcium carbonate and calcium oxalate precipitates were found to absorb the beta-particles emitted by the calcium 45. The calcium oxalate precipitates absorbed a few more per cent of the radiations than the carbonate precipitates of corresponding weight. This difference became greater as the weight of the precipitates increased. The self-absorption curves for both compounds show a nearly linear dependence upon sample weights in the range investigated in this study. Some writers (*2, 5*) have pointed out the desirability of preparing precipitates of "infinite thickness" in which a negligible number of beta-particles reach the surface from the bottom of the sample. In such precipitates the observed counting rate is proportional to the specific activity.

As indicated in the self-absorption curves in Figure 1, the specific activity is approximately a linear function of the weight of the precipitate throughout the range investigated, and precipitates that weigh more than 80 mg. are difficult to filter and transfer by the technique used in this investigation. Therefore, it is believed by the authors that for practical routine analysis it is easier to make corrections for self-absorption by such curves as those presented in Figure 1 than to prepare and handle precipitates of "infinite thickness."

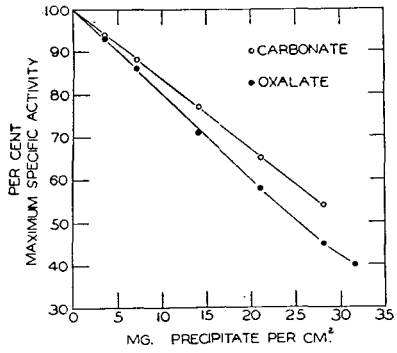

Figure 1. Beta-Particle Self-Absorption

Curves obtained with radioactive calcium oxalate and calcium carbonate precipitates

Interfering Elements. In biological materials the elements most likely to be present in sufficient quantities to interfere with either the carbonate or oxalate procedures are magnesium, aluminum, and phosphorus. Magnesium may be removed in the oxalate procedure by washing the precipitate with hot water (*1*). In the carbonate procedure 5 mg. of magnesium were found not to interfere in the weight of the precipitate, but caused a loss of approximately 25% of the radioactivity. The cause of this loss was not determined, but it may have been due to the magnesium altering the gross absorption coefficient so that the apparent activity was decreased by this amount. The oxalate method was not affected by 50 mg. of aluminum alone, but when this amount was present with 50 mg. of phosphorus, approximately twice the weight of precipitate was obtained as was expected from the amount of calcium present and there was a great decrease in the apparent specific activity of the precipitate. The increased weight of the precipitate was probably due to precipitation of aluminum phosphate. However, samples containing up to 20 mg. of both phosphorus and aluminum were found to have no interference. In the case of the calcium carbonate precipitation, 5 mg. of aluminum were without appreciable effect, but 50 mg. made filtration practically impossible. As little as 2 mg. of phosphorus caused interference in the carbonate method, particularly by increasing the time of filtration and decreasing the apparent specific activity of the precipitate.

Analysis of Biological Materials. In Table I data are presented that were obtained for (1) the per cent dose of calcium 45, and (2) the weight of total calcium found in equivalent aliquots of hen excrement by the oxalate and carbonate procedures. The metabolism studies made with the chickens using calcium 45 will be published elsewhere. The excrement samples were digested with concentrated nitric acid and made up to volume in volumetric flasks. Equivalent aliquots were taken for preparation of both the calcium oxalate and calcium carbonate precipitates. The values reported were calculated to represent the per cent of the administered calcium 45 excreted by the particular hen during the day that the excrement sample was collected. The hens had previously received single oral doses of the calcium 45 isotope.

The values obtained for per cent dose by the two procedures are nearly equivalent except sample 7, where 25.32% was obtained by the oxalate method, compared to 18.41% by the carbonate method. The carbonate procedure showed a little more total calcium to be present in the aliquots analyzed than was found by the oxalate method, except in samples 3 and 7, which were slightly lower. Although these data suggest that either method will give equivalent results on such biological materials as poultry excrement, because of the slow rate at which the carbonate solution filters, compared with that of the oxalate precipitate, the latter method is much to be preferred. Slow filtration was not experienced in the carbonate method on standard calcium samples that contained no added phosphorus or aluminum; this indicated that the carbonate procedure should find application in nonbiological materials or substances which do not contain significant quantities of interfering elements.

SUMMARY

Preparation of suitable precipitates for radioactivity assays of calcium 45 by the calcium oxalate and calcium carbonate methods was studied. The oxalate precipitate was found to have greater capacity to absorb beta-particles than the carbonate precipitate. This was expected because of the difference between the average atomic numbers of the two substances. The difference in self-absorption between the two types of precipitates is not great enough to affect size of samples required for routine analysis.

Table I. Calcium 45 and Weight of Total Calcium Found in Equivalent Aliquots of Hen Excrement

Sample No.	Oxalate Procedure		Carbonate Procedure	
	Dose, %	Ca, Mg.	Dose, %	Ca, Mg.
1	0.23	11.9	0.21	14.0
2	0.15	11.9	0.14	12.4
3	0.17	11.8	0.40	10.8
4	0.51	10.0	0.52	13.6
5	0.64	6.6	0.48	9.6
6	0.87	23.8	0.83	24.8
7	25.32	32.2	18.41	30.0

Interference of magnesium, phosphorus, and aluminum was studied in regard to weight of precipitate and influence on activity measurements. Magnesium altered the gross absorption coefficient of the carbonate precipitate, but otherwise caused no interference. Both phosphorus and aluminum markedly interfered with the rate of filtration of the carbonate solution in the carbonate method. Phosphorus caused a decrease in the apparent specific activity of the carbonate precipitate. In the case of the oxalate procedure, aluminum and phosphorus caused no interference when present alone, but when present together in the range of 50 mg. each, large discrepancies in weight of precipitate and in apparent specific activity were observed. Because of the common presence of interfering ions; the oxalate method is indicated to be more satisfactory than the carbonate procedure for the preparation of calcium precipitates for radioactivity assays, especially in biological materials.

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Analysis of East Texas Virgin Naphtha Fractions Boiling Up to 270° F.

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The individual paraffins and naphthenes in complex hydrocarbon mixtures boiling up to 270° F. can be determined by infrared spectroscopic procedures, combined with distillation and percolation methods. A method for the complete analysis of the individual C_7 and C_8 naphthenes boiling between 190° and 270° F. is reported for the first time. By applying these methods the compositions of two East Texas naphtha fractions boiling in the 115° to 215° F. and the 215° to 270° F. ranges have been determined. Quantitative data on 3 *n*-paraffins, 34 isoparaffins, 22 cyclopentane homologs, and 10 cyclohexane homologs are presented; these hydrocarbons comprise all the compounds of their respective types boiling up to 270° F., with the possible exception of some of the C_9 cyclopentane homologs.

THE determination of the composition of petroleum fractions is a major problem in studies directed toward the development of improved petroleum refining processes. It is well known that the reaction characteristics of hydrocarbons present in petroleum vary widely according to type, whether paraffin, naphthene, olefin, or aromatic, and to a lesser extent according to molecular weight. Reaction characteristics may also vary widely among structural isomers within a given homologous series of hydrocarbons. Methods for determining the composition of petroleum fractions, before and after processing, are of the utmost importance in guiding the decisions regarding the most favorable methods for processing these fractions.

Distillation and refractometric techniques have furnished the most complete data hitherto available on the composition of the paraffin-naphthene portions of virgin naphthas (*4, 7, 8*). Determinations of the C_1 through C_4 hydrocarbons are readily accomplished by distillation alone (*16*) or by means of mass spectrometry (*20*). The C_5 and C_6 hydrocarbons can be determined by means of distillation and refractive index measurements (*4, 8*). In the C_7 and higher boiling ranges, overlap between closely boiling isomers is encountered on distillation, and grouping of similar isomers in the analytical results is required, although some individual compounds boiling as high as 243° F. have been identified (*7*). Mass spectrometry has also been applied through the C_7 and higher fractions, although the grouping of various isomers having similar mass patterns is necessary (*2*).

The rapid determination of aromatic hydrocarbons present in gasoline fractions boiling up to 290° F. by ultraviolet or Raman spectrometric methods has been possible for some time (*6, 18*), and more recent extensions of the Raman technique have permitted determination of aromatic compounds boiling up to 350° F. or higher (*3, 11*). Infrared spectrometric procedures have been applied to the analysis of light hydrocarbons (*1*) and of paraffin mixtures boiling up to 255° F., but application of quantitative infrared techniques to the naphthenes has been limited to cyclopentane, methylcyclopentane, cyclohexane, and methylcyclohexane (*5, 10, 12*).

The infrared spectra of most of the naphthene isomers in the 120° to 270° F. range are now available from the National Bureau of Standards, A.P.I. Project 44, and the absorption bands best suited for distinguishing some of the di- and trisubstituted cyclopentanes and cyclohexanes have been reported (*15*).

The first part of the present paper describes infrared procedures by which the paraffin-naphthene portion of virgin naphthas may be analyzed quantitatively for all compounds boiling up to 270° F. The various compounds are determined on a volume per cent basis. The analysis distinguishes between all isomers, including *cis-* and *trans-*alkyl cyclopentanes and alkylcyclohexanes, with the exception of one pair of isomers for which the pure *cis-* and *trans-* isomers are not available (*cis-* and *trans-*1-methyl-3-ethylcyclopentane) and the tetramethylcyclopentanes, some of which may boil below 270° F.

The second part presents the quantitative analysis of the paraffin-naphthene portions of an East Texas light virgin naphtha for all compounds boiling up to 215° F., and of an East Texas heavy naphtha for compounds boiling up to 270° F. This represents an extension of approximately 30° F. above the highest boiling point for which the quantitative analysis of all the paraffins and naphthenes in crude oil had previously been reported (*19*).

INFRARED METHOD FOR DETERMINATION OF ALL PARAFFINS AND NAPHTHENES BOILING UP TO 270° F.

INFRARED ANALYSIS OF NAPHTHA CONSTITUENTS BOILING UP TO 215° F.

Infrared determination of the individual paraffins and naphthenes in naphtha feed and reaction products provides information on the behavior of the individual hydrocarbons. In this section of the paper, the determination of all compounds boiling up to 215° F. in the light naphtha range is described. By this method, the percentage of branched and straight-chain paraffins, cyclohexane, methylcyclohexane, and the alkylcyclopentanes, including the various dimethyl isomers, can be determined. Approximately 30 man-hours are required for the infrared analysis of the distillation cuts, including instrument and calculation time. The preparation of the sample, including percolation to remove the aromatics, distillation, and blending of the distillation cuts, requires approximately 120 hours of elapsed time.

Sample Preparation. The treatment of a virgin naphtha sample prior to infrared analysis insolves isolation of the paraffin-naphthene portion by percolation through silica gel, distillation into narrow boiling fractions, and the blending of distillation cuts into composite samples which can be analyzed by infrared techniques. The first step in this procedure, the segregation of the paraffins and naphthenes from the aromatics by a technique such as percolation, is necessary because the aromatics absorb strongly in the infrared regions in which the paraffins and naphthenes must be determined. Suitable percolation procedures include those by Mair and Forziati (*13*) and A.S.T.M. Designation D 936-47T. The aromatic fraction obtained by percolation is analyzed by ultraviolet techniques.

The paraffin-naphthene fraction should be distilled in a fractionating column of good separating efficiency. In these laboratories, satisfactory distillations are performed using an 80-plate Fenske-type column (*9*), operating at a boil-up rate of 150 ml. per hour, with a column holdup of 8 ml. The reflux ratios usually employed are 20 to 1 to 100° F., 50 to 1 to 150° F., and 100 to 1 thereafter to completion of a run.

Although narrow cuts (approximately 1%) are taken through-

Table I. Wave Lengths of Analytical Points Employed for Paraffins and Naphthenes in 80° to 215° F. Boiling Range

Compound	Wave Length, Microns		
	Absorption peak	Base line	
Isopentane	10.28	10.05	10.56
n-Pentane	13.75	13.29	14.03
Cyclopentane	11.19	10.77	11.70
2,2-Dimethylbutane	8.25	8.09	8.46
2,3-Dimethylbutane	8.87	8.36	9.13
2-Methylpentane	13.52	13.29	14.03
3-Methylpentane	10.50	10.31	10.66
n-Hexane	13.82	13.37	14.03
Methylcyclopentane	10.24	10.01	10.63
2,2-Dimethylpentane	13.51	13.32	13.98
2,4-Dimethylpentane	12.34	12.06	12.57
Cyclohexane	11.59	11.38	11.86
2,2,3-Trimethylbutane	9.20	9.10	9.45
3,3-Dimethylpentane	9.97	9.42	10.27
1,1-Dimethylcyclopentane	7.54	7.48	7.72
2,3-Dimethylpentane	8.93	8.50	9.13
2-Methylhexane	8.55	8.36	9.00
trans-1,3-dimethylcyclopentane	8.71	8.50	9.00
trans-1,2-dimethylcyclopentane	7.77	7.61	8.36
cis-1,3-dimethylcyclopentane	10.19	9.42	10.48
3-Methylhexane	13.56	13.29	13.98
3-Ethylpentane	11.11	10.75	11.33
n-Heptane	13.85	13.20	14.13
2,2,4-Trimethylpentane	8.02	7.89	8.13
cis-1,2-dimethylcyclopentane	9.64	9.46	10.05
Methylcyclohexane	11.84	11.35	11.98

out the distillation, the number of samples requiring infrared analysis is reduced by blending together those distillation cuts which contain the same components. The blending procedure is established by a consideration of the boiling point–refractive index data from the distillation and by infrared analysis of spot cuts. Whenever possible, blends are made between distillation plateaus formed by single hydrocarbons. By this procedure, the compounds boiling on the plateaus act as separating agents between lower and higher boiling compounds. In virgin naphtha analyses, however, twelve compounds boil in the 25° F. interval between 190° and 215° F., with no single component present in a sufficient quantity to form a distinct plateau. Consequently, several of the distillation cuts contain a large number of components. In this case, instead of blending all cuts of similar composition into a single, complex blend, several blends containing the same constituents and covering successive boiling range intervals are prepared. With this procedure, a check upon the analyses is furnished by the manner in which the concentrations of individual constituents increase and then decrease with increasing temperatures.

To complete the analysis of a light naphtha through 215° F., spot cuts selected beyond the methylcyclohexane plateau should be examined to ensure a determination of all the methylcyclohexane present in the sample.

Calibration. In the calibration of the infrared spectrometer to be used for this analysis, hydrocarbons of high purity such as those obtainable from the National Bureau of Standards, A.P.I. Project 46, should be employed. The spectrum of each compound in the 6.35- to 15-micron region is compared with those of other isomers in the same boiling range to select the absorption peak which is most nearly unique for distinguishing that compound from the constituents with which it is likely to occur. A base line method (*10*) is employed to obtain quantitative measurements of absorption peaks. The wave lengths selected for infrared analysis of the naphthenes and paraffins boiling from 82.1° to 213.7° F. are shown in Table I.

The data from these measurements of pure compounds are used to set up the simultaneous linear equations employed in performing analyses (*10*).

Analytical Accuracy. The accuracy of the determination of each of the compounds present in a particular naphtha may be established by the analysis of synthetic samples prepared from National Bureau of Standards pure hydrocarbons to match the composition of key distillation blends. In general, the accuracy which can be anticipated for analysis of distillation blends within the light naphtha boiling range is indicated by the data on synthetic blends shown in Table II, in which the blended and analyzed compositions of a number of synthetic samples are pre-

Table II. Infrared Analysis of Naphthene-Paraffin Synthetic Blends in 177° to 215° F. Boiling Range

Compound	B.P., ° F.	Synthetic 1			Synthetic 2					Synthetic 3			
		Blended comp., vol. %	Numerical Deviations		Blended comp., vol. %	Numerical Deviations				Blended comp., vol. %	Numerical Deviations		
			Run I, 9/4[a]	Run II, 3/4		Run I, 6/4	Run II, 6/7	Run III, 6/8	Run IV, 12/3	Run V, 12/8		Run I, 9/2	Run II, 9/3	Run III, 5/18
Cyclohexane	177.3	29.3	−1.2	−2.0	...	...	...	...	...	...	...	...	...	...
2,2,3-Trimethylbutane	177.6	0	No evidence		...	...	...	...	...	...	...	...	...	...
3,3-Dimethylpentane	186.9	0	No evidence		...	...	...	...	...	...	...	...	...	...
1,1-Dimethylcyclopentane	190.1	17.6	+1.1	+0.1	...	...	...	...	...	...	...	...	...	...
2,3-Dimethylpentane	193.6	23.5	−0.1	+0.9	9.6	−0.6	−1.0	−0.2	0.0	+0.2	...	...	...	...
2-Methylhexane	194.1	23.4	−0.9	+1.2	14.4	+0.1	−0.3	−0.1	+0.6	+0.5	...	...	...	...
trans-1,3-dimethylcyclopentane	195.4	6.2	+1.1	−0.2	19.1	+2.7	+1.5	+0.5	0.0	−1.3	...	...	...	...
trans-1,2-dimethylcyclopentane	197.4	...	...	...	14.4	+1.5	+0.8	+2.3	+0.1	+0.4	...	...	...	...
cis-1,3-dimethylcyclopentane	197.4	...	...	...	9.1	−5.9	−3.1	−2.8	−2.6	−0.9	...	...	...	...
3-Methylhexane	197.5	...	...	...	14.4	0.0	−0.1	−0.9	+1.5	+2.1	...	...	...	...
3-Ethylpentane	200.2	...	...	...	0			No evidence			...	...	...	...
n-Heptane	209.2	...	...	...	14.4	+0.7	+0.7	+1.0	+0.6	+1.6	59.0	+1.3	+2.3	−2.2
2,2,4-Trimethylpentane	210.6	...	...	...	0			No evidence			5.7	+2.9	+2.3	−2.1
cis-1,2-dimethylcyclopentane	211.2	...	...	...	4.6	+1.5	+1.5	+0.2	−0.2	−2.6	29.4	−2.7	−1.6	+0.6
Methylcyclohexane	213.7	...	...	...	...	...	...	...	...	...	5.9	−1.5	−3.0	+3.7

[a] Date indicates day upon which spectrum was obtained.

sented for comparison. These data indicate a mean deviation of ±1.3%. The maximum deviation is −5.9% on *cis*-1,3-dimethylcyclopentane, which suffers from strong interference from *trans*-1,3- and *trans*-1,2-dimethylcyclopentane and other isomers boiling within a few degrees. Because the compounds are analyzed in distillation blends which represent a small percentage of the total sample, the concentrations of the individual compounds calculated on a total sample basis should show a proportionally smaller deviation from the correct value.

INFRARED ANALYSIS OF NAPHTHA CONSTITUENTS BOILING FROM 215° TO 270° F.

Infrared techniques and distillation procedures have been extended to permit the analysis of hydrocarbon mixtures for all the C_8–C_9 paraffins and C_8 naphthenes falling in the 215° to 270° F. boiling range. This analysis is based on an extension of the principles described in the previous section. Because of the presence of a larger number of isomers for a comparable spread in boiling points, however, the procedure is more complex and time-consuming than for the light naphtha analysis.

Sample Preparation. For separation of the paraffins and naphthenes (obtained by percolation) in the heavy naphtha range, a distillation column of highest obtainable efficiency is recommended.

At these laboratories, a 200-plate Fenske-type column, operating with a boil-up rate of 100 ml. per hour and a holdup of 30 ml., is employed. The reflux ratio is maintained at 50 to 1 to 228° F. and 200 to 1 for the remainder of the distillation. If it is necessary to shut down the equipment before completion of the distillation, a still of this type should be placed on total reflux for at least 7 hours before continuing the distillation. In the boiling range from 240° to 250° F. where there are a large number of closely boiling isomers, the distillation is more difficult. In this region spot-cut infrared analyses of 2-ml. samples taken at 4-hour intervals (200 to 1 reflux) show a decrease in the amount of high-boiling isomers for two or three cuts after starting the take-off. In this range, the minimum time to reach equilibrium is estimated to be 18 hours.

In establishing the sample blending procedure, a number of individual distillation fractions are examined qualitatively by infrared. In the distillation of virgin naphtha fractions in the 215° to 270° F. range, the risers in the distillation curve are composed of ten to twelve compounds, separated by plateaus containing six to eight components. Because of the complexity of these mixtures, it is necessary to limit the blending to very closely boiling fractions and to analyze several blends including the same isomers. By this procedure the changes observed in the ratios of closely boiling isomers in successive distillation cuts can be used to check the quantitative results. Some of the individual fractions examined qualitatively as spot cuts may be subsequently blended with adjacent fractions, using aliquot portions, to reduce the number of quantitative analyses required.

Infrared Measurements and Calculations. Nearly all hydrocarbon standards needed for calibration in the 215° to 270° F. range can be obtained from the National Bureau of Standards, A.P.I. Project 46. The only compounds within this boiling range not available in high purity from any source include the *cis*- and *trans*-1-methyl-3-ethylcyclopentanes and *cis,cis,cis*-1,2,4-trimethylcyclopentane. The first two are available as an unseparated mixture, and the *cis,cis,cis*-1,2,4-trimethylcyclopentane is available as a concentrate in *cis,cis,trans*-1,2,4-trimethyl-*trans*-cyclopentane.

None of the tetramethylcyclopentanes are available. The boiling points of these compounds have not been determined, except for 1,1,2,3-tetramethylcyclopentane which boils at 271° F. It is probable that one or more of the isomers in this series boil below 270° F.

In performing the calibration for this analysis, the spectrum of each compound is measured in a rock salt cell 0.08 mm. thick. The wave lengths of the absorption bands and the respective base line points for this analysis are listed in Table III. In establishing analytical points for analyses in the heavy naphtha boiling range, base lines covering much wider wave-length intervals than those for the light naphtha analysis must be employed.

Because many of the compounds have relatively low infrared absorption with no unique peaks, often two and sometimes three wave-length positions are employed in determining a single compound. The equations for the analysis are set up in the manner described above for the light naphtha procedure. As many as twenty equations in eleven unknowns must be solved in the analysis of some distillation blends. When more than one

Table III. Wave Lengths of Infrared Analytical Points Employed for Determination of Paraffins and Naphthenes in 215° to 270° F. Boiling Range

Compound	Wave Lengths, Microns		
	Peak	Base Line	
Ethylcyclopentane	10.71	10.55	11.01
1,1,3-Trimethylcyclopentane	7.63	7.52	7.80
	10.08	9.78	10.73
2,2-Dimethylhexane	13.72	13.34	13.96
2,5-Dimethylhexane	10.86	10.60	11.08
cis,trans,cis-1,2,4-trimethylcyclopentane	8.69	8.41	9.00
2,4-Dimethylhexane	13.04	12.69	13.26
2,2,3-Trimethylpentane	9.24	9.08	9.46
cis,trans,cis-1,2,3-trimethylcyclopentane	10.11	9.51	10.73
	10.44	9.51	10.73
3,3-Dimethylhexane	12.78	12.58	13.00
2,3,4-Trimethylpentane	8.91	8.68	9.04
	9.62	9.51	10.73
1,1,2-Trimethylcyclopentane	9.47	9.29	9.62
2,3,3-Trimethylpentane	8.66	8.52	8.83
	9.94	9.51	10.73
2,3-Dimethylhexane	8.88	8.52	9.10
	13.51	13.17	14.11
2-Methyl-3-ethylpentane	11.52	11.28	11.83
cis,cis,trans-1,2,4-trimethylcyclopentane	9.82	9.50	10.12
	10.26	10.08	10.44
2-Methylheptane	8.56	8.41	9.04
	13.82	13.17	14.11
cis,cis,trans-1,2,3-trimethylcyclopentane	9.25	9.11	9.46
	9.93	9.50	10.12
4-Methylheptane	10.46	10.19	10.76
	13.51	13.17	14.11
3,4-Dimethylhexane	8.92	8.27	9.12
	10.53	9.51	10.73
cis,cis,cis-1,2,4-trimethylcyclopentane	8.98	8.27	9.12
	9.80	9.33	10.12
3-Methyl-3-ethylpentane	11.37	11.08	11.68
3-Ethylhexane	11.25	11.08	11.68
3-Methylheptane	10.37	9.51	10.73
	13.76	13.32	14.11
trans-1,4-dimethylcyclohexane	9.72	9.51	10.73
	10.08	9.51	10.73
1,1-Dimethylcyclohexane	8.52	8.27	9.12
	10.39	9.51	10.73
cis-1,3-dimethylcyclohexane	8.99	8.27	9.12
	10.52	9.51	10.73
	11.76	11.48	11.95
cis-1-methyl-3-ethylcyclopentane / *trans*-1-methyl-3-ethylcyclopentane	10.67	9.51	10.76
trans-1,2-methylethylcyclopentane	10.34	9.51	10.76
	10.99	10.80	11.11
1,1-Methylethylcyclopentane	10.04	9.51	10.76
	12.78	12.56	13.28
2,2,4,4-Tetramethylpentane	8.04	7.82	8.41
	10.26	9.38	10.56
cis,cis,cis-1,2,3-trimethylcyclopentane	9.20	8.96	9.38
	9.60	8.38	10.56
trans-1,2-dimethylcyclohexane	10.33	9.51	10.73
	11.30	11.08	11.52
2,2,5-Trimethylhexane	8.03	7.82	8.45
	8.33	7.82	8.45
cis-1,4-dimethylcyclohexane	9.13	8.96	9.38
	9.98	9.38	10.66
trans-1,3-dimethylcyclohexane	11.64	11.35	12.01
	11.91	11.35	12.01
n-Octane	13.87	13.20	14.13
Isopropylcyclopentane	7.58	7.51	7.82
	8.59	8.27	8.75
2,2,4-Trimethylhexane	8.05	7.87	8.45
cis-1,2-methylethylcyclopentane	10.68	10.55	10.91
cis-1,2-dimethylcyclopentane	9.95	9.68	10.41
	10.22	9.68	10.41
2,4,4-Trimethylhexane	8.58	8.27	8.75
	9.91	9.38	10.66
	10.21	9.38	10.66
2,2-Dimethylheptane	8.05	7.82	8.45
	10.31	9.38	10.66
n-Propylcyclopentane	11.23	10.87	11.71
	13.52	13.20	14.13
2,3,5-Trimethylhexane	8.66	8.27	9.12
	8.85	8.27	9.12
Ethylcyclohexane	11.25	11.08	11.71
	11.88	11.68	12.01

Table IV. Infrared Analysis of Synthetic Blends Matching East Texas Virgin Naphtha Paraffin-Naphthene Fractions in 214° to 270° F. Boiling Range

Compound	B.P., ° F.	Synthetic 4			Synthetic 5			Synthetic 6			Synthetic 7					
		Blended comp., vol. %	Numerical Deviations		Blended comp., vol. %	Numerical Deviations		Blended comp., vol. %	Numerical Deviations		Blended comp., vol. %	Numerical Deviations				
			Run I, 7/26[a]	Run II, 8/17		Run I, 7/22	Run II, 8/14		Run I, 7/26	Run II, 8/17		Run I, 8/16	Run II, 8/19	Run III, 12/1	Run IV, 12/6	Run V, 12/14
Methylcyclohexane	213.7	49.5	−1.0	+1.7	0.0	(−0.5)[b]	(−0.5)[b]	...	...	...	...	...	...	...	...	...
Ethylcyclopentane	218.2	18.1	+0.5	−1.5	3.3	+1.0	+1.1	...	...	...	...	...	...	...	...	...
1,1,3-Trimethylcyclopentane	220.8	32.4	+0.5	−0.2	7.1	−1.6	−2.0	...	...	...	4.9	−1.5	−1.5	+3.1	−0.2	−4.9
2,2-Dimethylhexane	224.3	...	...	...	1.0	−0.5	−0.7	...	...	...	...	...	...	...	...	...
2,5-Dimethylhexane	228.4	...	...	...	12.9	+0.1	−0.1	9.9	−0.1	+0.3	5.0	+0.3	+0.5	0.0	+0.7	+0.7
cis,trans,cis-1,2,4-trimethylcyclopentane	228.7	...	...	...	48.8	+1.0	+2.3	39.9	+1.6	−1.1	9.8	+1.4	−1.1	−4.0	+0.1	−0.2
2,4-Dimethylhexane	229.0	...	...	...	15.9	−0.5	−1.2	15.0	−0.5	−1.3	4.0	−1.0	−0.3	+2.7	+0.8	+1.9
2,2,3-Trimethylpentane	229.7	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
cis,trans,cis-1,2,3-trimethylcyclopentane	230.7	...	...	...	11.0	+0.5	−0.6	35.2	−1.0	−0.1	35.2	+1.3	+2.7	+0.7	+1.5	+2.8
3,3-Dimethylhexane	233.6	...	...	...	...	...	...	...	...	...	6.0	+0.6	−0.9	−1.0	−0.2	+0.9
2,3,4-Trimethylpentane	236.3	...	...	...	...	...	...	...	...	...	5.0	+0.3	−0.4	−0.1	−0.5	−0.9
1,1,2-Trimethylcyclopentane	236.7	...	...	...	...	...	...	...	...	...	6.0	−1.3	−1.6	−3.4	−3.7	−1.8
2,3,3-Trimethylpentane	238.6	...	...	...	...	...	...	...	...	...	2.0	−0.1	+0.3	+1.2	−0.8	−2.0
2,3-Dimethylhexane	240.1	...	...	...	...	...	...	...	...	...	19.1	+1.0	+3.7	+3.7	+5.3	+5.5
2-Methyl-3-ethylpentane	240.2	...	...	...	...	...	...	...	...	...	3.0	−0.9	−1.4	−3.0	−3.0	−2.0

Compound	B.P., ° F.	Synthetic 8		Synthetic 9		Synthetic 10					Synthetic 11		
		Blended comp., vol. %	Numerical Deviations, Run I, 8/31	Blended comp., vol. %	Numerical Deviations, Run I, 9/1	Blended comp., vol. %	Numerical Deviations				Blended comp., vol. %	Numerical Deviations	
							Run I, 8/16	Run II, 8/19	Run III, 12/1	Run IV 12/7		Run I, 8/27	Run II, 8/30
2,5-Dimethylhexane	228.4	...	...	1.1	−0.2	...	...	...	...	...	...	...	...
cis,trans,cis-1,2,4-trimethylcyclopentane	228.7	...	...	1.2	−1.1	...	...	...	...	...	...	...	...
2,4-Dimethylhexane	229.0	...	...	2.2	−0.1	...	...	...	...	...	...	...	...
2,2,3-Trimethylpentane	229.7	...	...	...	...	...	...	...	...	...	...	...	...
cis,trans,cis-1,2,3-trimethylcyclopentane	230.7	...	...	11.9	−0.5	0.8	−1.3	−0.5	−0.7	−1.3	...	...	...
3,-Dimethylhexane	233.6	...	...	2.3	+0.1	...	...	...	...	...	...	...	...
2,3,4-Trimethylpentane	236.3	...	...	2.3	+0.3	3.2	0.0	+0.6	+0.3	+0.7	...	...	...
1,1,2-Trimethylcyclopentane	236.7	24.4	+1.7	19.3	+1.9	4.1	+0.2	+0.7	+1.1	+0.5	...	...	...
2,3,3-Trimethylpentane	238.6	...	...	...	...	...	...	...	...	...	...	...	...
2,3-Dimethylhexane	240.1	44.2	−0.4	35.0	+2.7	27.9	+2.0	+1.2	+1.4	+1.2	3.9	+2.6	+1.2
2-Methyl-3-ethylpentane	240.2	14.4	−1.2	11.3	−2.8	8.9	−2.2	−2.1	−3.5	−4.3	0.0	(−0.9)[b]	(−0.7)
cis,cis,trans-1,2,4-trimethylcyclopentane	242.1	...	...	...	...	0.0	(−6.5)	(−4.5)	(−5.4)	(−7.4)	0.0	(−3.9)	(−1.3)
2-Methylheptane	243.8	17.0	−0.9	13.4	+0.7	42.5	−0.9	−0.7	+0.8	+0.3	73.2	+0.5	+0.5
cis,cis,trans-1,2,3-trimethylcyclopentane	243.9	...	...	...	...	0.0	(−1.2)	(−1.9)	(−4.4)	(−4.6)	4.0	−0.6	−1.8
4-Methylheptane	243.9	...	...	...	...	6.8	+0.3	0.0	+0.6	+0.4	15.0	−2.8	−2.3
3,4-Dimethylhexane	243.9	...	...	...	...	5.8	+1.5	+0.8	+0.5	+2.6	3.9	+0.3	+1.0
cis,cis,cis-1,2,4-trimethylcyclopentane	244	...	...	...	...	...	...	...	...	...	...	...	...
3-Methyl-3-ethylpentane	244.9	...	...	...	...	...	...	...	...	...	0.0	(−1.0)	(−1.2)
3-Ethylhexane	245.4	...	...	...	...	...	...	...	...	...	0.0	(−0.6)	(−2.3)
3-Methylheptane	246.1	...	...	...	...	...	...	...	...	...	0.0	(−0.7)	(+1.4)
trans-1,4-dimethylcyclohexane	246.8	...	...	...	...	...	...	...	...	...	0.0	(−0.1)	(−0.3)

Compound	B.P., ° F.	Synthetic 12					Synthetic 13			Synthetic 14			Synthetic 15		
		Blended comp., vol. %	Numerical Deviations				Blended comp., vol. %	Numerical Deviations		Blended comp., vol. %	Numerical Deviations		Blended comp., vol. %	Numerical Deviations	
			Run I, 8/26	Run II, 8/20	Run III, 12/1	Run IV, 12/7		Run I, 3/1	Run II, 3/2		Run I, 3/1	Run II, 3/3		Run I, 3/1	Run II, 3/2
2-Methylheptane	243.8	17.0	−0.6	−1.3	−1.4	−1.7	...	...	...	...	...	...	...	...	...
cis,cis,trans-1,2,3-trimethylcyclopentane	243.9	0.0	(−7.4)	(−4.5)	(−2.5)	(−3.0)	...	...	...	...	...	...	...	...	...
4-Methylheptane	243.9	6.0	−2.1	−2.9	0.0	−1.6	...	...	...	...	...	...	...	...	...
3,4-Dimethylhexane	243.9	1.0	+0.2	+0.2	+1.5	+1.8	...	...	...	...	...	...	...	...	...
cis,cis,cis-1,2,4-trimethylcyclopentane	244	...	...	...	...	...	...	...	...	...	...	...	...	...	...
3-Methyl-3-ethylpentane	244.9	2.0	+0.4	+0.4	−0.2	+1.0	...	...	...	...	...	...	...	...	...
3-Ethylhexane	254.4	0.0	(+0.4)	(−0.1)	(−0.2)	(+0.2)	...	...	...	...	...	...	...	...	...
3-Methylheptane	246.1	37.1	+1.2	+2.2	−2.3	+1.5	...	...	...	...	...	...	...	...	...
trans-1,4-dimethylcyclohexane	246.8	19.1	+1.4	+1.0	+2.1	+1.2	10.0	+1.9	+1.2	...	...	...	...	...	...

Compound	B.P., ° F.	Synthetic 12 Blended comp., vol. %	Synthetic 12 Numerical Deviations Run I, 8/26	Synthetic 12 Numerical Deviations Run II, 8/20	Synthetic 12 Numerical Deviations Run III, 12/1	Synthetic 12 Numerical Deviations Run IV, 12/7	Synthetic 13 Blended comp., vol. %	Synthetic 13 Numerical Deviations Run I, 3/1	Synthetic 13 Numerical Deviations Run II, 3/2	Synthetic 14 Blended comp. vol., %	Synthetic 14 Numerical Deviations Run I, 3/1	Synthetic 14 Numerical Deviations Run II, 3/3	Synthetic 15 Blended comp. vol. %	Synthetic 15 Numerical Deviations Run I, 3/1	Synthetic 15 Numerical Deviations Run II, 3/2
1,1-Dimethylcyclohexane	247.2	3.0	−0.7	−0.5	+1.4	−1.0	3.0	−1.0	−0.5	...	...	...	...	...	...
cis-1,3-dimethylcyclohexane	248.2	13.9	+0.1	+0.5	−2.2	−1.6	49.0	+1.6	0.1	0.0	(+0.5)	(+1.1)	...	...	...
cis-1-methyl-3-ethylcyclopentane	248.4														
trans-1-methyl-3-ethylcyclopentane	249.4	1.0	−0.4	+0.6	+1.1	+0.4	12.0	−3.5	−1.5	3.9	−0.8	−0.3	...	...	...
trans-1,2-methylethylcyclopentane	250.1	...	...	...	...	...	26.0	+0.9	+0.6	4.0	−4.2	−4.0	...	...	...
1,1-Methylethylcyclopentane	250.7	...	...	...	...	...	0.0	(−0.4)	(−0.4)	2.0	3.9	+4.3	...	...	...
2,2,4,4-Tetramethylpentane	252.1	...	...	...	...	...	...	...	...	...	...	...	...	...	...
cis,cis,cis-1,2,3-trimethylcyclopentane	253.4	...	...	...	...	...	...	...	...	2.0	+0.1	+0.4	0.0	(−0.6)	(−1.9)
trans-1,2-dimethylcyclohexane	254.2	...	...	...	...	...	...	...	...	63.1	−2.5	−3.5	3.1	−0.4	−0.2
2,2,5-trimethylhexane	255.4	...	...	...	...	...	...	...	...	0.0	...	...	0.0	...	...
cis-1,4-dimethylcyclohexane	255.8	...	...	...	...	...	...	...	...	7.0	−2.1	−1.6	3.0	+0.2	−0.2
trans-1,3-dimethylcyclohexane	256.0	...	...	...	...	...	...	...	...	12.0	+2.2	+2.7	5.2	+0.4	+0.9
n-Octane	258.2	...	...	...	...	...	...	...	...	6.0	+2.7	+0.9	88.7	−0.2	−0.5

Compound	B.P., ° F.	Synthetic 16 Blended comp., vol. %	Synthetic 16 Numerical Deviations, Run I, 3/3	Synthetic 17 Blended comp., vol. %	Synthetic 17 Numerical Deviations, Run I, 3/3
n-Octane	258.2	85.1	−3.0	20.0	+2.6
Isopropylcyclopentane	259.5	0.0	(−1.4)	0.0	(−1.1)
2,2,4-Trimethylhexane	259.8	0.0	(+3.0)	0.0	(+0.5)
cis-1,2-methylethylcyclopentane	262.4	0.0	(+0.9)	5.0	−2.0
cis-1,2-dimethylcyclohexane	265.5	10.0	+0.6	20.0	−2.7
2,4,4-Trimethylhexane	266.5	0.0	(−2.3)	0.0	(−3.0)
2,2-Dimethylheptane	267.4	1.0	−2.1	5.0	+0.9
n-Propylcyclopentane	267.7	1.0	−3.4	10.0	−0.4
2,3,5-Trimethylhexane	268.5	0.0	(−5.0)	0.0	(−3.7)
Ethylcyclohexane	269.2	3.0	+0.5	40.0	+1.0

[a] Date indicates day upon which spectrum was obtained.
[b] Deviations included in parentheses refer to compounds which were not present in synthetic samples but were included in analytical calculations because their absence could not be established by qualitative analysis.

equation is employed for a single constituent, these equations are carried along as a group. An average of the concentrations obtained is carried forward during the approximation procedure and the final average is taken as the proper concentration for that constituent.

Analytical Accuracy. In order to check the accuracy of the determination of each of the compounds found present, a series of synthetic samples, prepared to match the calculated composition of key fractions selected from the analysis, should be analyzed by infrared spectrometry. A careful comparison of the spectra of corresponding synthetic blends and samples furnishes a check against the presence of unidentified material in the samples. The quantitative infrared analyses of a series of synthetic samples, presented in Table IV, indicate that the maximum deviation in determining the concentration of hydrocarbons in the 215° to 270° F. is usually less than ±3% from the actual amount present, with a mean deviation of ±1.4%. This accuracy is considered excellent in view of the small differences in the infrared spectra of compounds in the blends, many of which contain eleven or twelve components.

High negative values instead of zeros are obtained for the *cis, cis, trans* isomers of 1,2,3- and 1,2,4-trimethylcyclopentane in several of the synthetic blends. The absorption peaks of these isomers are relatively weak and occur at wave lengths where interference from the other compounds is strong. In general, the infrared spectra of the cyclopentane series tend to become more diffuse as the number of alkyl groups on the nucleus increases. This trend is not so evident for the cyclohexane series.

INFRARED ANALYSIS

The particular naphthas for which the compositions are reported here were obtained from two separate distillations of an East Texas crude oil. The lower boiling or "light" naphtha was distilled in a refinery pipe still containing approximately 30 plates. The nominal boiling range of this part of the naphtha was from the initial to 250° F., and the total distillate collected represented 14.5% of the crude oil charged. The higher boiling or "heavy" naphtha was obtained from a pilot plant distillation, which was carried out with approximately the same efficiency as the pipe still operation. The nominal cut temperatures for the heavy naphtha distillation were 215° and 435° F., with a reported total of 24.5% of the crude oil charge taken as overhead.

In the analytical distillation of these naphthas, carried out in columns of high efficiency, it was found that 13.3% of the light naphtha boils above 247° F. and that approximately 6% of the heavy naphtha boils below 215° F.

EAST TEXAS LIGHT VIRGIN NAPHTHA, 115° TO 215° F. FRACTION

The analytical results on individual distillation blends for the East Texas light virgin naphtha are shown in Table V. The accuracy of the analysis for each of the compounds pres-

Table V. Composition of Narrow Boiling Fractions, Paraffin-Naphthene Portion of East Texas Light Virgin Naphtha

(Volume per cent by infrared analysis. Individual cuts from 80-plate distillation at 100 to 1 reflux. Initial to 147° F. at 50 to 1)

Cut No.		0–7	8–10	11–12	13–17	18–22	23	24–29	30–34	35	36–38	39–41	42	43–47	48–49	50–51	52–54	56–61	62–63	64	65–70	71	Bottoms
Cut temperature, ° F.		197	121	139	144	156	157	162	179	180	195	196	197	198	199	207	209	213	214	214	234	241	
Cut volume, %		12.73	3.36	2.30	5.60	5.77	1.29	6.78	5.61	1.12	3.81	3.48	1.18	5.71	2.30	2.08	3.42	7.84	2.30	1.12	6.79	1.23	14.18
Cumulative volume, %		12.73	16.09	18.39	23.99	29.76	31.05	37.83	43.44	44.56	48.37	51.85	53.03	58.74	61.04	63.12	66.54	74.38	76.68	77.80	84.59	85.82	100.00
Compounds boiling below 82.1° F.	B.P., ° F.		[a]																				
Isopentane	82.1	100	4	3	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
n-Pentane	96.9		85	13	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Cyclopentane	120.7		10	29	3	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
2,2-Dimethylbutane	121.5		...	5	1	0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
2,3-Dimethylbutane	136.4		...	0	13	4	1	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
2-Methylpentane	140.5		...	0	37	73	9	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
3-Methylpentane	145.9		...	0	0	16	39	2	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
n-Hexane	155.7		...	...	...	3	50	98	59	1	...	...	...	...	...	...	...	...	...	...	...	...	...
Methylcyclopentane	161.3		...	...	...	...	...	...	39	70	...	...	...	...	...	...	...	...	...	...	...	...	...
2																							
2,2-Dimethylpentane	174.6		...	...	...	...	...	2	1	3	...	...	...	...	...	...	...	...	...	...	...	...	...
2,4-Dimethylpentane	176.9		...	...	...	...	...	0	4	7	...	...	...	...	...	...	...	...	...	...	...	...	...
Cyclohexane	177.3		...	...	...	...	...	No evidence	24	90	35	1	...	...	...	...	...	...	...	...	...	...	...
2,2,3-Trimethylbutane	177.6		...	...	...	...	...	...	No evidence		0	0	...	...	...	...	...	...	...	...	...	...	...
3,3-Dimethylpentane	186.9		...	...	...	...	...	...	...	...	3	2	...	...	...	...	...	...	...	...	...	...	...
1,1-Dimethylcyclopentane	190.1		...	...	...	...	...	...	...	...	23	13	...	...	...	...	...	...	...	...	...	...	...
2,3-Dimethylpentane	193.6		...	...	...	...	...	...	...	...	9	13	8	6	3	3	...	...	...	...	...	...	...
2-Methylhexane	194.1		...	...	...	...	...	...	...	...	17	31	24	13	3	1	0	...	...	...	...	...	...
trans-1,3-dimethylcyclopentane	195.4		...	...	...	...	...	...	...	...	6	22	23	20	10	8	0	...	...	...	...	...	...
trans-1,2-dimethylcyclopentane	197.4		...	...	...	...	...	...	...	...	5	10	18	28	36	28	6	3	...	...	...	...	...
cis-1,3-dimethylcyclopentane	197.4		...	...	...	...	...	...	...	...	0	0	5	7	10	1	0	0	...	...	...	...	...
3-Methylhexane	197.5		...	...	...	...	...	...	...	...	2	8	18	24	30	21	9	3	...	...	...	...	...
3-Ethylpentane	200.2		...	...	...	...	...	...	...	...	...	...	No evidence	0	Trace	5	Trace	...	...	...	...	...	...
n-Heptane	209.2		...	...	...	...	...	...	...	...	...	...	3	0	1	27	81	48	4	1	...	...	...
2,2,4-Trimethylpentane	210.6		...	...	...	...	...	...	...	...	...	...	Qualitative examination indicates absence								...	...	...
cis-1,2-dimethylcyclopentane	211.2		...	...	...	...	...	...	...	...	...	...	0	1	6	4	1	5	7		...	...	...
Methylcyclohexane	213.7		...	...	...	...	...	...	...	...	...	...	1	1	1	2	3	41	89	98	35	0	...
Compounds boiling above 213.7° F.		...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1	65	100	100

[a] Leaders indicate that presence of compound was not expected, and no analysis for it was carried out.

ent is established by the analysis of synthetic samples prepared to match the composition of key distillation blends. Such data, as shown in Table II, indicate a mean deviation of ±1.3% for all compounds determined and a maximum deviation of −5.9% on *cis*-1,3-dimethylcyclopentane, which suffers from strong interference. Inasmuch as the distillation blends which were analyzed in this case represented from 7 to 32% of the total sample, the concentrations of the individual compounds calculated on the total sample (initial to 250° F. light naphtha) basis should show an average deviation within 0.1 to 0.4% from the correct value.

The infrared analysis of the East Texas paraffin-naphthene fraction and the ultraviolet analysis of the aromatics present, calculated on the initial to 250° F. sample basis, are presented in Table VI. With the exception of 2,2,3-trimethylpentane and 2,2,4-trimethylpentane, all the paraffin, alkylcyclopentane, and alkylcyclohexane isomers boiling between 80° and 215° F. have been identified in the sample. The relative amounts of the various types of hydrocarbons in the C_6 and C_7 ranges are shown in Table VII.

EAST TEXAS HEAVY VIRGIN NAPHTHA, 215° TO 270° F. FRACTION

The fractions of the East Texas heavy virgin naphtha analyzed by infrared spectrometry represent 31% of the paraffin-naphthene portion of the heavy naphtha or 6.6% of the original East Texas crude oil. They cover the temperature range from 194° to 270° F. The aromatic content of the total (215° to 435° F.) heavy naphtha, determined by Raman spectroscopy, was 13%, corresponding to 3.2% of the crude oil.

The initial analytical distillation required 339 hours on heat to reach 35% off at 281° F. In this distillation, while column operating conditions were being established, several column floods and incipient floods occurred in the region between 240° and 250° F., where there are a large number of closely boiling isomers. A second distillation was therefore carried out, and the analytical data on the cuts from the two distillations were combined on the normal octane plateau. A total of 41 samples were analyzed quantitatively, of which 19 were in the 240° to 250° F. interval.

The analyses of the individual naphtha fractions and blends covering the 190° to 270° F. boiling range are presented in Tables VIII to XI. In addition to the known paraffins and naphthenes included in these tables, an unknown compound which boils above 259° F. was detected in maximum concentration near 262° F. Inasmuch as the extraneous absorption peaks appearing in the spectra of the cuts containing this material suggest the presence of a naphthene, the unknown may be one of the tetramethylcyclopentanes. The boiling points of these compounds, except for 1,1,2,3-tetramethylcyclopentane which boils at 271° F., have not been established. The

Table VI. Composition of East Texas Light Virgin Naphtha

(Initial to 250° F. nominal boiling range, 14.5% of crude. Volume per cent of paraffins and naphthenes by infrared analysis, aromatics by ultraviolet analysis)

Compound	B. P., °F.	Percentage of Naphtha	Percentage of Crude
Compounds boiling below 120° F.		15.8	2.28
Cyclopentane	120.7	1.2	0.18
2,2-Dimethylbutane	121.5	0.2	0.03
2,3-Dimethylbutane	136.4	0.6	0.08
2-Methylpentane	140.5	5.4	0.78
3-Methylpentane	145.9	3.1	0.45
n-Hexane	155.7	8.2	1.19
Methylcyclopentane	161.3	6.5	0.94
2,2-Dimethylpentane	174.6	0.2	0.03
Benzene	176.2	0.3	0.04
2,4-Dimethylpentane	176.9	0.3	0.04
Cyclohexane	177.3	3.6	0.56
2,2,3-Trimethylbutane	177.6	0.0	0.00
3,3-Dimethylpentane	186.9	0.2	0.03
1,1-Dimethylcyclopentane	190.1	1.3	0.19
2,3-Dimethylpentane	193.6	1.3	0.19
2-Methylhexane	194.1	2.8	0.40
trans-1,3-Dimethylcyclopentane	195.4	2.7	0.40
trans-1,2-Dimethylcyclopentane	197.4	4.1	0.60
cis-1,3-Dimethylcyclopentane	197.4	0.7	0.10
3-Methylhexane	197.5	3.5	0.51
3-Ethylpentane	200.2	0.1	0.01
n-Heptane	209.2	7.1	1.03
2,2,4-Trimethylpentane	210.6	0.0	0.00
cis-1,2-Dimethylcyclopentane	211.2	0.9	0.12
Methylcyclohexane	213.7	8.8	1.27
Nonaromatics above 213.7° F.		19.4	2.81
Toluene	231.1	1.7	0.25
		100.0	14.48

Table VII. Relative Amounts of C_6 and C_7[a] Naphthenes and Paraffins in East Texas Light Virgin Naphtha

(Volume per cent by infrared analysis. Total volume, 61.6% on total light naphtha fraction. Initial to 250° F. nominal boiling range, 14.5% of crude)

	Percentage of C_6 and C_7 Paraffin-Naphthene Portion	Percentage of Crude
n-Hexane	13.3	1.19
n-Heptane	11.5	1.03
Isohexanes	15.0	1.34
Isoheptanes	13.7	1.21
Total paraffins	53.5	4.77
Methylcyclopentane	10.5	0.94
Dimethylcyclopentanes	15.8	1.41
Cyclohexane	5.9	0.53
Methylcyclohexane	14.3	1.27
Total naphthenes[a] through 215° F.	46.5	4.15

[a] These figures do not include ethylcyclopentane boiling at 218.2° F.

possibility of the presence of peroxides and olefins has been eliminated by chemical tests, and other oxygenated materials and aromatics may be ruled out on the basis of the infrared data.

The percentages of each compound, calculated on the basis of the 215° to 435° F. paraffin-naphthene portion and on the total crude, are shown in Table XII. As demonstrated in Table IV, analyses of synthetic blends, prepared to match the calculated composition of key fractions, indicate that the maximum deviation in determining the concentrations of hydrocarbons in distillation blends in the 215° to 270° F. range is usually less than ±3% from the actual amounts present, with a mean deviation of ±1.4%. On the basis of the 215° to 435° F. naphtha sample, the mean deviations expected for the concentrations of individual constituents lie between 0.01% and 0.1%.

The C_8 paraffins, constituting 10.2% of the total heavy naphtha, were principally *n*-octane and methylheptanes, as shown in Table XIII. Fifteen of the 18 octane isomers were found in the sample, although the identification of 2,2-dimethylhexane and 3-methyl-3-ethylpentane is questionable, because the maximum concentration found for each in any fraction was 1%. The three isomers which appeared to be definitely absent, or present in less than detectable amounts, were 2,2,3,3-tetramethylbutane and 2,2,3- and 2,2,4-trimethylpentane.

The distribution of the C_8 alkylcyclopentanes, comprising 10.2% of the total heavy naphtha sample, is summarized in Table XIV. Of the 21 isomers, only the *cis,cis,cis*-1,2,4-trimethylcyclopentane was not detected. Compounds for which identification is questionable include 1,1-methylethylcyclopentane, *cis*-1,2-methylethylcyclopentane, isopropylcyclopentane, and *cis,cis,cis*-1,2,3-trimethylcyclopentane. The *cis,cis,trans*-1,2,3- and *cis,cis,trans*-1,2,4-trimethylcyclopentane were probably present in higher concentrations than are reported, as indicated by the results on synthetic blend analyses.

The ratio of the lower to higher boiling isomer of each cis-trans pair of dimethylcyclohexanes is about 5 to 1. In conformity with the conclusions of recent investigators (*14, 17*), the lower boiling 1,2- and 1,4-dimethylcyclohexanes have been called "trans," while the lower boiling 1,3-dimethylcyclohexane has been called "cis." On this basis, the 1,3-dimethylcyclohexanes are the only

Table VIII. Composition of Narrow Boiling Fractions, Paraffin-Naphthene Portion of East Texas Heavy Virgin Naphtha

(Volume per cent by infrared analysis. Cuts from 200-plate distillation at 200 to 1 reflux. Initial to 228° F. at 50 to 1)

Cut No.		1	2	3–5	6–11	12	13–17
Cut temperature, ° F.		194	197	210	213	214	22
Cut volume, %		0.46	0.50	1.45	2.75	0.47	2.36
Cumulative volume, %		0.46	0.96	2.41	5.16	5.63	7.99
	B.P., ° F.						
C_6 and lighter material		100	...	...	...	...	...
1,1-Dimethylcyclopentane	190.1	[a]	8	...	...	...	...
2,3-Dimethylpentane	193.6	...	9	2	...	...	...
2-Methylhexane	194.1	...	24	4	...	...	...
trans-1,3-dimethylcyclopentane	195.4	...	20	9	...	...	...
trans-1,2-dimethylcyclopentane	197.4	...	19	21	...	...	...
cis-1,3-dimethylcyclopentane	197.4	...	5	4	...	...	...
3-Methylhexane	197.5	...	14	20	No evidence	...	...
3-Ethylpentane	200.2	...	No evidence		...	...	...
n-Heptane	209.2	...	1	36	43	...	...
2,2,4-Trimethylpentane	210.6	...	...	No evidence		...	...
cis-1,2-dimethylcyclopentane	211.2	...	...	2	10	...	...
Methylcyclohexane	213.7	...	...	2	47	100	52
Ethylcyclopentane	218.2	...	...	...	...	...	11
1,1,3-Trimethylcyclopentane	220.8	...	...	...	...	...	20
2,2-Dimethylhexane	224.3	...	...	...	...	...	0
2,5-Dimethylhexane	228.4	...	...	...	...	...	4
cis,trans,cis-1,2,4-trimethylcyclopentane	228.7	...	...	...	...	...	11
2,4-Dimethylhexane	229.0	...	...	...	...	...	1
2,2,3-Trimethylpentane	229.7	...	...	...	...	...	...

[a] Leaders indicate that presence of a given compound was not expected and no analysis was carried out.

Table IX. Composition of Narrow Boiling Fractions, Paraffin-Naphthene Portion of East Texas Heavy Virgin Naphtha

(Volume per cent by infrared analysis. Cuts from 200-plate distillation at 200 to 1 reflux. Initial to 228° F. at 50 to 1)

Cut No.		18–23	24	25–26	27–28	29	30	31–33	34	35 37–38	36	39–42
Cut temperature, ° F.		230	233	239	241	244	244	245	245	245	246	246
Cut volume, %		1.54	0.25	0.50	0.48	0.23	0.24	0.70	0.25	0.73	0.24	0.94
Cumulative volume, %		9.53	9.78	10.28	10.76	10.99	11.23	11.93	12.18	13.15		14.09
	B.P., ° F.											
Methylcyclohexane	213.7	0	[a]	...	...	...	...	...	...	...	...	...
Ethylcyclopentane	218.2	1	...	...	...	...	...	...	...	...	...	...
1,1,3-Trimethylcyclopentane	220.8	0	1	...	...	...	...	...	...	...	...	...
2,2-Dimethylhexane	224.3	1	No evidence	...	...	...	...	...	...	...	...	...
2,5-Dimethylhexane	228.4	10	3	0	...	...	...	...	...	...	...	...
cis,trans,cis-1,2,4-trimethylcyclopentane	228.7	35	5	0	...	...	...	...	...	...	...	...
2,4-Dimethylhexane	229.0	13	4	7	...	...	...	...	...	...	...	...
2,2,3-Trimethylpentane	229.7		No evidence		...	...	...	...	...	...	...	...
cis,trans,cis-1,2,3-trimethylcyclopentane	230.7	40	39	11	0	0	...	...	...	...	...	...
3,3-Dimethylhexane	233.6	0	5	3	0	0	...	...	...	...	...	...
2,3,4-Trimethylpentane	236.3	...	7	9	1	1	...	...	...	...	...	...
1,1,2-Trimethylcyclopentane	236.7	...	22	29	5	5	...	...	...	...	...	...
2,3,3-Trimethylpentane	238.6	...	3	5	0	2	...	...	...	...	...	...
2,3-Dimethylhexane	240.1	...	11	26	25	12	8	2	3	2	4	4
2-Methyl-3-ethylpentane	240.2	...	0	4	12	3	4	1	0	0	1	0
cis,cis,trans-1,2,4-trimethylcyclopentane	242.1	...	...	...	4	3	0	1	0	2	0	0
2-Methylheptane	243.8	...	...	6	40	59	70	73	72	64	55	55
cis,cis,trans-1,2,3-trimethylcyclopentane	243.9	...	...	...	3	3	2	3	4	3	1	6
4-Methylheptane	243.9	...	...	...	6	9	12	13	15	14	12	17
3,4-Dimethylhexane	243.9	...	...	...	4	3	4	6	4	7	6	3
cis,cis,cis-1,2,4-trimethylcyclopentane	244	...	...	...	...	...	...	...	...	...	Possible trace	
3-Methyl-3-ethylpentane	244.9	...	...	...	...	...	0	0	0	0	1	0
3-Ethylhexane	245.4	...	...	...	...	...	0	0	0	1	4	3
3-Methylheptane	246.1	...	...	...	...	...	0	1	2	6	12	11
trans-1,4-dimethylcyclohexane	246.8	...	...	...	...	...	0	0	0	1	4	1

Cut No.		43	44–50	51	53	52 54–56 58–59	57	60	61–62	63	64–65	66
Cut temperature, ° F.		246	249	249	249	249	249	249	250	250	251	251
Cut volume, %		0.23	1.76	0.23	0.24	1.45	0.25	0.26	0.49	0.23	0.50	0.23
Cumulative volume, %		14.32	16.08	16.31		18.25		18.51	19.00	19.23	19.73	19.96
	B.P., ° F.											
2-Methylheptane	243.8	47	16	0	[a]	...	...	...	...	...	...	...
cis,cis,trans-1,2,3-trimethylcyclopentane	243.9	8	0	0	...	...	...	...	...	...	...	...
4-Methylheptane	243.9	15	4	0	...	...	...	...	...	...	...	...
3,4-Dimethylhexane	243.9	4	3	0	...	...	...	...	...	...	...	...
cis,cis,cis-1,2,4-trimethylcyclopentane	244	Possible trace		...	...	...	...	...	...	...	...	...
3-Methyl-3-ethylpentane	244.9	0	0	0	...	...	...	...	...	...	...	...
3-Ethylhexane	245.4	2	6	3	4	2	1	...	...	...	...	...
3-Methylheptane	246.1	20	35	30	33	24	22	14	11	6	2	...
trans-1,4-dimethylcyclohexane	246.8	2	16	24	26	27	30	27	23	19	16	10
1,1-Dimethylcyclohexane	247.2	0	3	5	6	6	7	6	5	5	3	3
cis-1,3-dimethylcyclohexane	248.2	2	16	36	29	36	39	50	57	57	60	49
cis-1-methyl-3-ethylcyclopentane	248.4	{0	{1	{2	{2	{5	{1	{1	{1	{9	{3	{12
trans-1-methyl-3-ethylcyclopentane	249.4											
trans-1,2-methylethylcyclopentane	250.1	...	...	0	0	0	...	2	3	4	14	26
1,1-Methylethylcyclopentane	250.7	...	...	0	0	0	...	0	0	0	2	0
2,2,4,4-Tetramethylpentane	252.1	...	...	...	...	...	...	...	...	...	...	No evidence
cis,cis,cis-1,2,3-trimethylcyclopentane	253.4	...	...	...	...	...	...	...	...	...	...	No evidence

[a] Leaders indicate that presence of a given compound was not expected and no analysis was carried out.

Table X. Composition of Narrow Boiling Fractions, Paraffin-Naphthene Portion of East Texas Heavy Virgin Naphtha

(Volume per cent by infrared analysis. Cuts from 200-plate distillation at 200 to 1 reflux. Initial to 228° F. at 50 to 1)

Cut. No.		67–72	73–74	75–80	81–87	88–95	96–100	101–103
Cut temperature, ° F.		255	255	258	259	259	260	268
Cut volume, %		1.43	0.48	1.42	1.73	1.97	1.19	0.73
Cumulative volume, %		21.39	21.87	23.29	25.02	26.99	28.18	28.91
	B.P., °F.							
3-Methylheptane	246.1	0	[a]	...	...	...	...	...
trans-1,4-dimethylcyclohexane	246.8	0	...	...	...	...	...	...
,1-Dimethylcyclohexane	247.2	0	...	...	...	...	...	...
cis-1,3-dimethylcyclohexane	248.2	16	1	0	...	...	...	...
cis-1-methyl-3-ethylcyclopentane	248.4	{13	{5	{0	...	...	...	...
trans-1-methyl-3-ethylcyclopentane	249.4							
trans-1,2-methylethylcyclopentane	250.1	24	3	0	...	...	...	...
1,1-Methylethylcyclopentane	250.7	3	1	3	...	...	...	...
2,2,4,4-Tetramethylpentane	252.1	...	...	...	...	...	...	...
cis,cis,cis-1,2,3-trimethylcyclopentane	253.4	0	2	0	0	...	...	...
trans-1,2-dimethylcyclohexane	254.2	40	67	32	2	0	...	...
2,2,5-Trimethylhexane	255.4	...	...	...	...	...	...	...
cis-1,4-dimethylcyclohexane	255.8	2	7	9	3	1	...	...
trans-1,3-dimethylcyclohexane	256.0	2	11	19	5	1	...	...
n-Octane	258.2	...	3	37	90	98	Est. 87	Est. 23
Isopropylcyclopentane	259.5	...	...	...	...	...	...	+ higher
2,2,4-Trimethylhexane	259.8	...	...	...	...	...	...	boiling
cis-1,2-methylethylcyclopentane	262.4	...	...	...	...	...	...	compounds
Unknown (tetramethylcyclopentane?)							Present	

[a] Leaders indicate that presence of a given compound was not expected and no analysis was carried out.

Table XI. Composition of Narrow Boiling Fractions, Paraffin-Naphthene Portion of East Texas Heavy Virgin Naphtha

(Volume per cent by infrared analysis. Cuts from 200-plate distillation at 200 to 1. Initial to 228° F. at 50 to 1)

Cut No.		95-99[a]	100-102	103-106	107-109	110-111	112-117
Cut temperature, ° F.		259	264	269	272	272	278
Cut volume, %		1.27	0.84	1.00	0.75	0.50	1.61
Cumulative volume, %		27.26	28.10	29.10	29.85	30.35	31.96
	B.P., ° F.						
n-Octane	258.2	91	68	12	1	...	...
Isopropylcyclopentane	259.5	2	2	2	0	...	...
2,2,4-Trimethylhexane	259.8	0	0	0	1	...	...
cis-1,2-methylethylcyclopentane	262.4	4	1	3	0	...	...
Unknown (tetramethylcyclopentene?)	...	3	12	20	Trace	...	...
cis-1,2-dimethylcyclohexane	265.5	[b]	5	17	4	...	...
2,4,4-Trimethylhexane	266.5	...	4	0	4	...	...
2,2-Dimethylheptane	267.4	...	1	4	0	5	...
n-Propylcyclopentane	267.7	...	0	9	12	9	...
2,3,5-Trimethylhexane	268.5	...	0	0	0	1	...
Ethylcyclohexane	269.2	...	2	33	78	77 + Higher boiling compounds	Est. 25 + Higher boiling compounds

[a] Cuts in this table are from a different distillation from that reported in Table X. Two distillations were required because flooding of distillation column was encountered in first distillation.
[b] Leaders indicate that presence of a given compound was not expected and no analysis was carried out.

Table XII. Composition of Paraffin-Naphthene Portion of East Texas Heavy Virgin Naphtha

(215° to 435° F. nominal boiling range, 21.3% of crude. Volume per cent by infrared analysis)

Compound	B.P., ° F.	% of Paraffin-Naphthene Portion	% of Crude	Compound	B.P., ° F.	% of Paraffin-Naphthene Portion	% of Crude
C_6 and lighter material		0.46	0.098	4-Methylheptane	243.9	0.60	0.128
1,1-Dimethylcyclopentane	190.1	0.04	0.008	3,4-Dimethylhexane	243.9	0.24	0.051
2,3-Dimethylpentane	193.6	0.07	0.015	*cis,cis,cis*-1,2,4-trimethylcyclopentane	244	[a]	0.000
2-Methylhexane	194.1	0.18	0.038	3-Methyl-3-ethylpentane	244.9	0.00	0.000
trans-1,3-dimethylcyclopentane	195.4	0.23	0.048	3-Ethylhexane	245.4	0.20	0.043
trans-1,2-dimethylcyclopentane	197.4	0.40	0.085	3-Methylheptane	246.1	1.51	0.322
cis-1,3-dimethylcyclopentane	197.4	0.08	0.017	*trans*-1,4-dimethylcyclohexane	246.8	1.22	0.260
3-Methylhexane	197.5	0.36	0.077	1,1-Dimethylcyclohexane	247.2	0.26	0.055
3-Ethylpentane	200.2	0.00	0.000	*cis*-1,3-dimethylcyclohexane	248.2	2.24	0.477
n-Heptane	209.2	1.71	0.364	*cis*-1-methyl-3-ethylcyclopentane	248.4	0.38	0.081
2,2,4-Trimethylpentane	210.6	0.00	0.000	*trans*-1-methyl-3-ethylcyclopentane	249.4		
cis-1,2-dimethylcyclopentane	211.2	0.30	0.064	*trans*-1,2-methylethylcyclopentane	250.1	0.52	0.111
Methylcyclohexane	213.7	3.02	0.644	1,1-Methylethylcyclopentane	250.7	0.10	0.021
Ethylcyclopentane	218.2	0.28	0.060	2,2,4,4-Tetramethylpentane	252.1	0.00	0.000
1,1,3-Trimethylcyclopentane	220.8	0.50	0.107	*cis,cis,cis*-1,2,3-trimethylcyclopentane	253.4	0.01	0.002
2,2-Dimethylhexane	224.3	0.02	0.004	*trans*-1,2-dimethylcyclohexane	254.2	1.38	0.294
2,5-Dimethylhexane	228.4	0.26	0.055	2,2,5-Trimethylhexane	255.4	0.00	0.000
cis,trans,cis-1,2,4-trimethylcyclopentane	228.7	0.81	0.173	*cis*-1,4-Dimethylcyclohexane	255.8	0.26	0.055
2,4-Dimethylhexane	229.0	0.27	0.058	*trans*-1,3-dimethylcyclohexane	256.0	0.46	0.098
2,2,3-Trimethylpentane	229.7	0.00	0.000	*n*-Octane	258.2	5.23	1.115
cis,trans,cis-1,2,3-trimethylcyclopentane	230.7	0.77	0.164	Isopropylcyclopentane	259.5	0.06	0.013
3,3-Dimethylhexane	233.6	0.03	0.006	2,2,4-Trimethylhexane	259.8	0.01	0.002
2,3,4-Trimethylpentane	236.3	0.07	0.015	*cis*-1,2-methylethylcyclopentane	262.4	0.09	0.019
1,1,2-Trimethylcyclopentane	236.7	0.24	0.051	Unknown (tetramethylcyclopentane?)	...	0.47	0.100[b]
2,3,3-Trimethylpentane	238.6	0.04	0.009	*cis*-1,2-dimethylcyclohexane	265.5	0.24	0.051
2,3-Dimethylhexane	240.1	0.41	0.087	2,4,4-Trimethylhexane	266.5	0.06	0.013
2-Methyl-3-ethylpentane	240.2	0.10	0.021	2,2-Dimethylheptane	267.4	0.07	0.015
cis,cis,trans-1,2,4-trimethylcyclopentane	242.1	0.05	0.011	*n*-Propylcyclopentane	267.7	0.23	0.049
2-Methylheptane	243.8	2.72	0.580	2,3,5-Trimethylhexane	268.5	0.01	0.002
cis,cis,trans-1,2,3-trimethylcyclopentane	243.9	0.16	0.034	Ethylcyclohexane	269.2	1.72	0.367
				Total		31.15	6.637

[a] Presence not detected by analytical method employed.
[b] Amount determined by difference.

geometric isomers in the cyclopentane or cyclohexane series in which the *cis* form is found to predominate.

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Table XIII. Relative Amounts of C_8 Paraffins in East Texas Heavy Virgin Naphtha

(Volume per cent by infrared analysis)

	% of C_8 Paraffins[a]		% of Paraffin-Naphthene Portion[b]	
n-Octane	44.7		5.23	
Methylheptanes	41.3		4.83	
2-Methylheptane		23.3		2.72
3-Methylheptane		12.9		1.51
4-Methylheptane		5.1		0.60
Dimethylhexanes	10.5		1.23	
2,3-Dimethylhexane		3.5		0.41
2,4-Dimethylhexane		2.3		0.27
2,5-Dimethylhexane		2.2		0.26
3,4-Dimethylhexane		2.0		0.24
3,3-Dimethylhexane		0.3		0.03
2,2-Dimethylhexane		0.2		0.02
Trimethylpentanes	0.9		0.11	
2,3,4-Trimethylpentane		0.6		0.07
2,3,3-Trimethylpentane		0.3		0.04
2,2,3-Trimethylpentane		0.0		0.00
2,2,4-Trimethylpentane		0.0		0.00
Ethylhexane	1.7		0.20	
3-Ethylhexane		1.7		0.20
Methylethylpentanes	0.9		0.10	
3-Methyl-3-ethylpentane		0.9		0.10
3-Methyl-3-ethylpentane		0.0		0.00
Total	100.0		11.70	

[a] C_8 paraffins comprise 10.2% of total heavy naphtha (215 to 435° F. nominal boiling range), or 2.5% of crude.
[b] Paraffin-naphthene portion comprises 87% of total heavy naphtha (215° to 435° F. nominal boiling range), or 21.3% of crude.

Table XIV. Relative Amounts of C_8 Naphthenes in East Texas Heavy Virgin Naphtha

(Volume per cent by infrared analysis)

	% of C_8 Naphthenes[a]		% of Paraffin-Naphthene Portion[b]	
Trimethylcyclopentanes	21.7		2.54	
cis,trans,cis-1,2,4-trimethylcyclopentane		6.9		0.81
cis,cis,trans-1,2,4-trimethylcyclopentane		0.4		0.05
cis,cis,cis-1,2,4-trimethylcyclopentane		[c]		[c]
cis,trans,cis-1,2,3-trimethylcyclopentane		6.6		0.77
cis,cis,trans-1,2,3-trimethylcyclopentane		1.4		0.16
cis,cis,cis-1,2,3-trimethylcyclopentane		0.1		0.01
1,1,3-Trimethylcyclopentane		4.3		0.50
1,1,2-Trimethylcyclopentane		2.0		0.24
Methylethylcyclopentanes	9.3		1.09	
cis + *trans*-1,3-methylethylcyclopentanes		3.2		0.38
cis + *trans*-1,2-methylethylcyclopentanes		5.2		0.61
1,1-Methylethylcyclopentane		0.9		0.10
Propylcyclopentanes	2.5		0.29	
Isopropylcyclopentane		0.5		0.06
n-Propylcyclopentane		2.0		0.23
Dimethylcyclohexanes	51.8		6.06	
1,1-Dimethylcyclohexane		2.2		0.26
cis-1,2-dimethylcyclohexane		2.1		0.24
trans-1,2-dimethylcyclohexane		11.8		1.38
cis-1,3-dimethylcyclohexane		19.2		2.24
trans-1,3-dimethylcyclohexane		3.9		0.46
cis-1,4-dimethylcyclohexane		2.2		0.26
trans-1,4-dimethylcyclohexane		10.4		1.22
Ethylcyclohexane	14.7		1.72	
Total	100.0		11.70	

[a] C_8 naphthenes comprise 10.2% of total heavy naphtha (215–435° F. nominal boiling range), or 2.5% of crude.
[b] Paraffin-naphthene portion comprises 87% of total heavy naphtha (215–435° F. nominal boiling range), or 21.3% of crude.
[c] Presence not detected by analytical method employed.

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Sodium and Potassium Determination in Refractory Materials

Using Flame Photometer

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A method has been devised by which refractory materials are sintered with calcium carbonate as in the J. Lawrence Smith method, and sodium and potassium are determined on the water extract using the flame photometer. Consideration is given to the calcium present in the extract. Results are at least as accurate, and probably more accurate, as those obtained using the J. Lawrence Smith method, and the time necessary to complete the analysis is cut in half.

UNLESS thoroughly worked out for a specific material, the J. Lawrence Smith method for estimation of sodium and potassium in refractory materials is tedious and time-consuming, and the optimum conditions for the analysis may not be at once obtained. Various modifications of the method are given by Hillebrand and Lundell (*3*).

Several possible errors are inherent in this procedure. First, the analyst is not absolutely sure that the mixed chlorides obtained are free from elements other than sodium and potassium (and possibly, very minor amounts of lithium). Secondly, the amount of alkali chlorides obtained from the small sample (0.5 gram) normally used is often so very small that very slight errors in weight give noticeable errors in the results. Thirdly, sodium is usually obtained by difference; the potassium is determined, for instance, as chloroplatinate, on the mixed chlorides. Consequently, any error in the potassium determination is reflected in

the sodium figure obtained. This is particularly noticeable when much potassium and little sodium are present; indeed, the sodium figure in such a case may be 50% out. Such discrepancies have been noticed in the collaborative results given for sodium and potassium with such standard samples as those issued by the National Bureau of Standards. All in all, the results obtained by this method, unless followed with extreme precision and care, may well be looked upon with some suspicion. If the method has been thoroughly worked out and the procedure carefully followed for specific samples, good results are obtainable. Nevertheless, the method is time-consuming.

Table I. Comparison of J. Lawrence Smith and Modified Methods

(Single determinations)

	J. Lawrence Smith Method				Modified Method, Gravimetric and Flame Photometer					
		Gravimetric and Flame Photometer			1500 P.P.M. CaO		1800 P.P.M. CaO		N.B.S. Results	
Sample	Gravimetric as total chlorides, %	Na_2O, %	K_2O, %	Calcd. as total chlorides, %	Na_2O, %	K_2O, %	Na_2O, %	K_2O, %	Na_2O, %	K_2O, %
Celite 545	6.70	3.00	0.71	6.78	2.96	0.72	2.96	0.72	..	..
Celite Sil-O-Cel	2.48	0.60	0.56	2.02	0.58	0.57	0.59	0.50	..	..
Plastic clay	5.80	0.28	3.11	5.46	0.28	3.11	0.28	3.14	0.28	3.17
Opal glass	20.76	8.59	3.35	21.50	8.82	3.43	8.97	3.43	8.48	3.25
Borosilicate glass	7.98	4.05	0.17	7.91	4.15	0.18	4.19	0.18	4.16	0.16
J-M firebrick	4.04	0.88	1.43	3.93	0.88	1.44	0.88	1.44	..	..

It was felt that if the alkalies in refractory materials could be obtained in solution without too much trouble, the flame photometer could be employed for rather rapid determination of the alkalies separately. Such a method has been found and very satisfactory results have been obtained. Indeed, it is believed that, in general, more consistently accurate results can be obtained in not more than half the time necessary when using the complete J. Lawrence Smith method.

FLAME PHOTOMETER

The flame photometer used in this work was the Perkin-Elmer instrument, Model 52A. This has a dual optical system enabling the internal standard method to be employed; this reduces the effects of gas and air pressure fluctuations, foreign ions and molecules, and viscosity differences. The effects, and they are serious ones, produced by these conditions are discussed rather fully by Berry, Chappell, and Barnes (*1*) and by Parks, Johnson, and Lykken (*4*). The latter authors used the Perkin-Elmer Model 18, in which there is a single optical system, as did Bills, McDonald, Niedermeier, and Schwartz (*2*), who proposed to reduce errors by using a newly designed amplification circuit and by working at lower concentration ranges than have been recommended in the past. Using the same instrument, Pratt and Larson (*6*) suggested the use of interference filters to reduce error due to calcium in the determination of sodium.

It is not essential to use the internal standard method, particularly when specific conditions of the above-mentioned variables can be properly duplicated in samples and standards. Under certain conditions, as when small amounts of lithium may be present in the samples tested, the direct-reading method may be more accurate.

SAMPLES ANALYZED BY NEW METHOD

In order to try this method on different types of refractory materials, the materials listed in Table I were used. These included three National Bureau of Standards certified analysis samples in order to check the results obtained. The presence of small and large amounts of sodium and of potassium will be noticed. The borosilicate glass contained 12% B_2O_3. It was thought that these different samples fairly well represented the general run of refractory materials.

PREPARATION OF SOLUTIONS AND COMPENSATION FOR INTERFERENCE

In the proposed method, which employs the initial steps of the J. Lawrence Smith method, calcium and chloride are present in the solutions containing the alkalies. Using a 0.5-gram original sample, the extract containing the alkalies, after addition of sufficient lithium nitrate to act as internal standard at a final concentration of 100 p.p.m. as lithium, was bulked to 250 ml. Six refractory materials were treated in the same manner and the calcium was determined in each and in a blank run at the same time, after bulking to volume. Calculated as calcium oxide the amounts varied from 1530 to 1714 p.p.m., while the blank contained 1798 p.p.m. It was, therefore, necessary to add similar amounts of calcium as chloride to each of the standard solutions used. In order to note the effect of different amounts of calcium and whether the amount to be added to the standards was critical, two sets of standard solutions were made up, containing similar amounts of sodium and potassium as chlorides, but one set containing 1500 p.p.m. and the other set 1800 p.p.m. of calcium calculated as oxide.

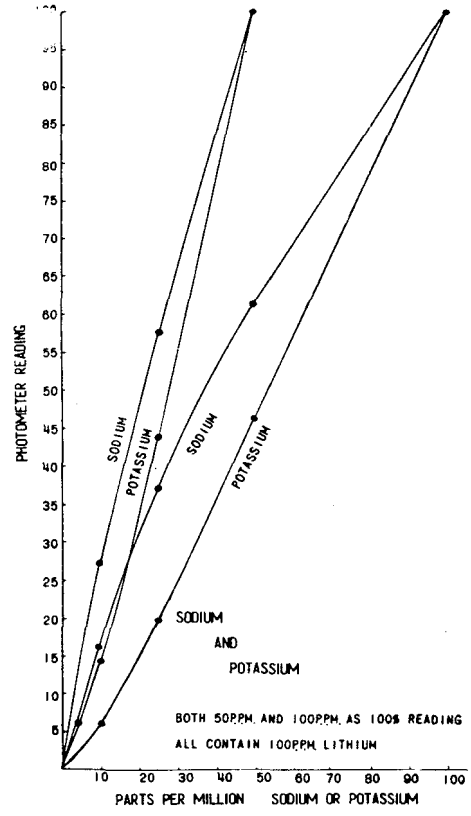

Figure 1

Results show that curves obtained with the standards coincided in the higher alkali ranges and were slightly separated, as would be expected, in the lower alkali ranges (Figure 2). Results obtained on the samples indicate that it made little, if any, difference which amount of calcium was present, as long as the appropriate curve was used with the standard solutions against which the samples were run. Hence, it appears that the amount of calcium present is not critical. It is best, of course, to keep it around the amount found in solution after known conditions of treatment and extraction of the treated sample. This can quickly be determined simply by making a calcium determination. In

Table II. Calcium in Extract Solutions (Bulked to 250 Ml.) in Modified Method

Sample	Calcium as CaO, P. P. M.
Celite 545	1530
Sil-O-Cel	1714
Plastic clay	1638
Opal glass	1544
Borosilicate glass	1682
J-M firebrick	1564
Blank	1798

all probability it would not be necessary to repeat this except under markedly different conditions.

PREPARATION OF CALIBRATION CURVES

The number of standard solutions required will depend on the amount of the alkalies present in the bulked sample solutions. These are made up in the usual manner and kept in No-Solvit (Wheaton & Company) or polythene bottles. Borosilicate glass may be used for several weeks without noticeably affecting the alkali contents even of sample solutions. To each standard, 100 p.p.m. of lithium are added as with the solutions, if the internal standard solution is used.

Calcium approximately equivalent to that present in the sample solutions must now be added. A stock solution of, say 10,000 p.p.m. of calcium as oxide, is made up by dissolving the equivalent of low-alkali C.P. calcium carbonate in just sufficient hydrochloric acid. The solution is heated gently to drive off carbon dioxide, cooled, and bulked to volume. After the requisite amounts of this stock solution have been added to the standards, it is made up to volume.

Photometer readings are made, either by the direct-reading or the internal standard method (*5*). The frequent checking of the instrument with the standards is essential. Curves should be made as indicated, the larger the number of curves with as large a number of points as possible, the better. In practice, the number of curves necessary will be limited to actual requirements.

Figures 1 and 2 show the curves made for use in this work.

PROCEDURE

As in the J. Lawrence Smith method, intimately mix 0.5 gram of finely powdered sample with 4 grams of low-alkali C.P. calcium carbonate and 0.5 gram of C.P. ammonium chloride. Heat in a special thimble crucible if available, or in a 30-ml. platinum crucible with a well-fitting lid, inserted in an asbestos board in the normal manner and for the usual time. Cool the crucible, transfer the complete contents to a well-used borosilicate glass beaker, and allow the sintered mass to disintegrate completely. Filter into a 250-ml. volumetric flask and wash well with hot water, using as little volume as is necessary. Depending upon the expected amount of alkali present, it may be advisable to use a 500-ml. or 1000-ml. volumetric flask. The calcium is present, in the main, as chloride with some hydroxide. To prevent precipitation of the hydroxide, neutralize with a few drops of hydrochloric acid. Using the same amounts of calcium carbonate and ammonium chloride, run a blank in an exactly similar manner. It is anticipated that with a final volume of 250 ml. and with careful and similar treatment and washing, the calcium content as oxide will range somewhere around 1500 to 1800 p.p.m. This work shows that standards made with either amount gave very comparable results.

Add sufficient lithium nitrate, if the internal standard method is used, to give an equivalent of 100 p.p.m. as lithium metal in the final solution. Because this is merely used as a reference standard, the actual amount added is not critical, but it is absolutely essential to add exactly similar quantities to all the samples and all the standards. Consequently, use stock solutions made so that at least 5 ml. can be measured exactly, preferably from a microburet. Bulk the sample solutions to volume. Read on the flame photometer and use the calibration curves to determine the alkali contents.

RESULTS

The results of the J. Lawrence Smith method taken to the total chlorides stage, flame photometer determination of sodium and potassium on these total chloride solutions, flame photometer determination of sodium and potassium obtained by the method given above, and National Bureau of Standards data for three of the six materials are all given in Table I. *In most cases the two* sets of flame photometer readings agree well among themselves and with the National Bureau of Standards results. The gravimetric chlorides figures given, although they agree with the other results fairly well, are probably somewhat less accurate for the reasons stated above. The photometer results are consistent, whereas the separate National Bureau of Standards results for sodium given on the certificate of analysis for the clay, which are averaged to give the final value, are not. In other words, the short flame photometer method may well give inherently more accurate results than the general run of good gravimetric work by the J. Lawrence Smith method. This is largely due to the fact that sodium is normally determined by difference in the latter method.

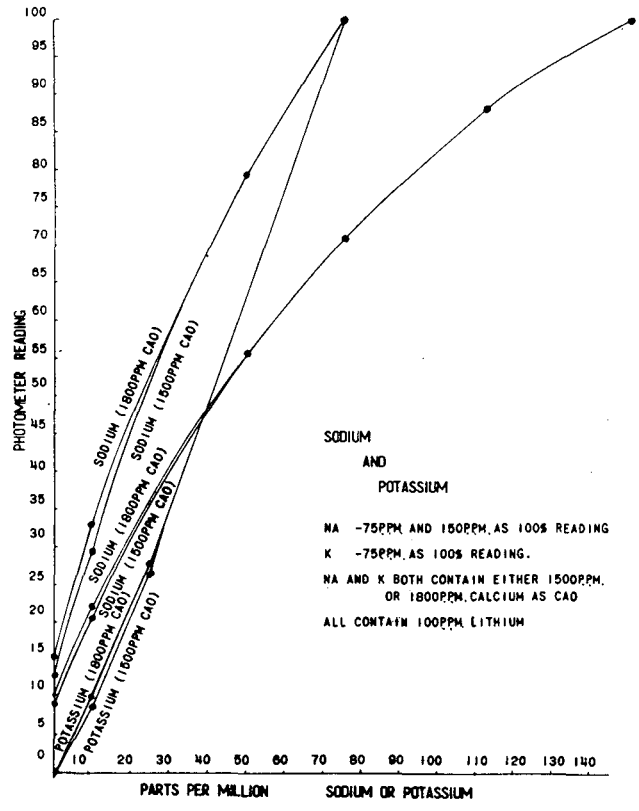

Figure 2

Table II shows the actual calcium as oxide found in the solutions and blank made up to 250 ml.

DISCUSSION

The possibility that ions other than the alkalies, calcium, and chloride might be present and so produce interference in the flame photometer should be considered. This possibility is, however, rather remote, for refractory materials do not normally contain soluble materials other than the alkalies, calcium, and magnesium. The method of treatment—sintering with calcium carbonate and ammoniun chloride—renders insoluble all metals other than the alkalies, calcium, and possibly minor amounts of magnesium, amounts that would have negligible effect on the flame photometer readings. Some sulfate as calcium sulfate might be present. However, sulfate is not usually present in refractory materials, and the solubility of calcium sulfate is

small. The presence of 12% boron as B_2O_3 in the borosilicate glass analyzed did not prevent accurate results from being obtained by this method.

The gas used with air in these experiments was acetylene. Substitution of propane, using an appropriate burner, might be of some advantage, as there would then be a lower rate of excitation of any nonalkali metals present. Sodium and potassium excite more readily than most other commonly present metals.

The photometer readings were made on the instrument without previously cleaning the burner which had been in use for some time. Although it is well always to keep the burner clean, the results obtained indicate that good work may be done even when the instrument is not in optimum condition.

It is important that the flow of air and of gas do not fluctuate during the readings. To this end it is advisable to insert a manometer in each line. If the air is supplied from an air pump, the presence of a large vessel in the line will help to equalize pressure.

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Hafnium-Zirconium and Tantalum-Columbium Systems

Quantitative Analysis by X-Ray Fluorescence

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The x-ray fluorescence analysis method was adapted to the determination of small amounts of hafnium in zirconium and tantalum in columbium. Curves of the relative intensity of spectral lines of tantalum and columbium or hafnium and zirconium were plotted against percentage composition by using prepared standard compositions. As an example of the accuracy attainable, with a counting time of 3 to 5 minutes on a 0.5 atomic % specimen of tantalum in columbium, the probable error in tantalum content due to statistical fluctuations of the Geiger counter was 0.02% or 4% of the amount present.

QUANTITATIVE analysis of the hafnium-zirconium and tantalum-columbium systems is difficult by standard chemical methods. It is also somewhat difficult by spectrochemical means; however, Feldman (*3*) has recently published very good data on spectrochemical analysis of samples containing less than 1% by weight of hafnium in zirconium. Most present interest lies in the low-hafnium or -tantalum end of these systems. Hafnium usually occurs as small impurity of about 1.5 weight % in zirconium deposits and is very difficult to separate from the zirconium. X-ray analysis has been used extensively for the analysis of the hafnium-rich end of the hafnium-zirconium system since the discovery of hafnium by Coster and von Hevesy (*2*). Its application to the hafnium-poor end of the system is shown in this paper.

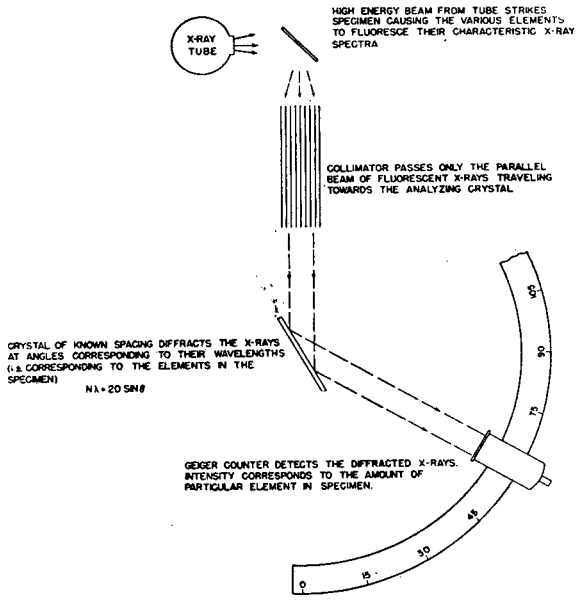

Figure 1. Principles of X-Ray Fluorescence Analysis Method

Hafnium was discovered by its x-ray *L* spectrum when a sample of zircon was placed on the target of an x-ray tube and excited by electron bombardment. Placing the specimen on the target of a demountable tube is inconvenient, however, With the development of the x-ray fluorescence method (*4*) where the specimen is outside the tube, the procedure is simpler and faster. The principles of x-ray fluorescence are shown in Figure 1. The method has proved valuable in measuring the small concentrations of lead and bromine in gasoline and in similar problems and would seem to be directly applicable to the small concentrations of hafnium in zirconium or tantalum in columbium. Usually there is no overlapping of the x-ray spectral lines from elements with similar chemical properties because they fall in the same column of the periodic table and the difference in atomic number is such that the x-ray spectra are well separated. However, in the hafnium-zirconium and tantalum-columbium systems, the difference in atomic number is such that the *K* series spectrum of zirconium diffracted in the second order by the crystal overlaps somewhat the *L* series spectrum of hafnium. The same is true of columbium and tantalum. Therefore, the method of analysis was more complicated than with most systems. The wave lengths of

the spectral lines of the elements in the two systems are shown in Figure 2.

Recently Cauchois and Mac Taggart (*1*) described a method for analysis by x-ray absorption where the absorption was measured on both sides of the absorption edge of hafnium. They did not give the results of the experiment or indicate the accuracy

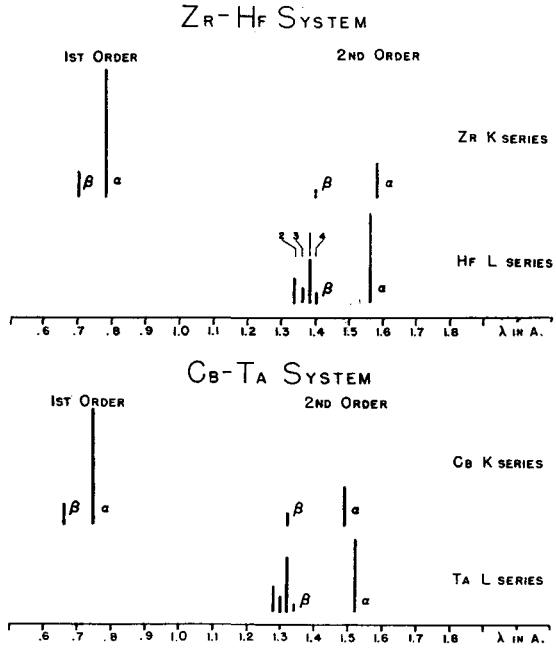

Figure 2. Spectra of Elements in Hafnium-Zirconium and Tantalum-Columbium Systems

Lengths of lines are only an approximate representation of relative intensities.

possible. Zemany, Winslow, Poellmitz, and Liebhafsky have also reported on the use of x-ray absorption for the analysis of a hafnia-zirconia mixture (*5*). However, they were working with percentages of hafnia above 20%.

APPARATUS

The x-ray fluorescence analysis unit was essentially that described by Friedman and Birks (*4*), with slight modification in the method of specimen mounting and replacement of the spectrometer arc with a diffraction-type spectrometer in which the Geiger counter was geared to move at twice the speed of the crystal. As is shown in Figure 1, the beam from the x-ray tube strikes the specimen, causing it to fluoresce the characteristic x-ray spectra of the elements. A beam of parallel fluorescent radiation coming off the specimen is passed through the collimator and diffracted according to its wave length by the crystal and the intensity is measured by the Geiger counter with standard scaling circuits.

EXPERIMENTAL METHODS

The overlapping of the spectra complicated the experimental procedure, but three methods of attacking the problem were tried with comparable accuracy of results: Method A, fine collimation to resolve the overlapped hafnium and zirconium lines; Method B, comparison of the integrated intensity of an unresolved tantalum-columbium doublet with the integrated intensity of a resolved columbium line; Method C, lowering the x-ray tube voltage to excite the hafnium *L* spectrum without exciting the zirconium *K* spectrum. It might seem advantageous at first thought to raise the tube voltage high enough to excite the *K* spectrum of hafnium and so avoid the overlap with zirconium. However, this would require power of the order of 80 kv., which is not attainable with the commercial diffraction type of x-ray power supplies or tubes. The wave length of Hf$K\alpha$ is 0.22 A., which would require an analyzing crystal with a spacing of the order of 1 A., such as one of the weaker planes in quartz.

TANTALUM-COLUMBIUM SYSTEM

C.P. filings of tantalum and columbium metals were converted to the pentoxides by heating. The columbium contained less than 1% of tantalum and the tantalum contained even less columbium. Standards were prepared by adding tantalum to columbium in amounts of 0.5, 1, 2, and 4.5 atomic % and the x-ray spectra were plotted from 6 to 19 degrees θ with a sodium chloride crystal.

Figure 3 shows the spectrum of the columbium standard and of the mixture with 4.5 atomic % tantalum. The curve in Figure 4 was obtained by Method B by taking the ratio of the area of the unresolved doublet of Ta$L\beta$ plus Cb$K\beta$ to the area of the first order of Cb$K\alpha$—that is, the ratio of A/B in Figure 3. Figure 4 is the standard curve for the tantalum-columbium system and depends on the fact that all other elements which would give spectral lines near *A* or *B* have been removed. Such a separation is not difficult and would be necessary for almost any method of analysis. In fluorescence analysis, the metal atoms fluoresce independently of the compound in which they are present. The nature of the compound therefore does not affect the line intensity or position, except for a very small second-order effect on the intensity due to the small absorption of the oxygen or other nonmetallic atoms in the compound. Thus the same calibration curve would be equally valid for the sulfide, nitride, or silicate, because it is based on the atomic per cent of tantalum in columbium.

The accuracy of the data depends on the number of counts measured by the Geiger counter. Other causes of inaccuracy, such as voltage fluctuations and circuit irregularities, have been reduced to well below the statistical accuracy of the Geiger

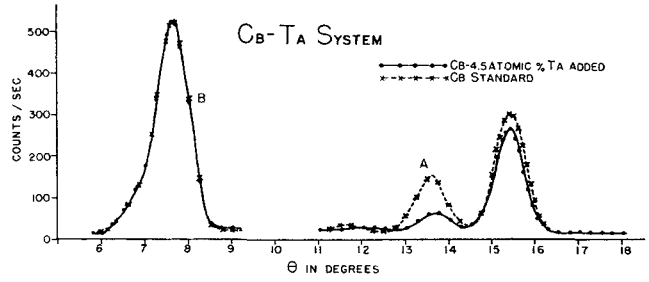

Figure 3. Representative Spectra of Tantalum-Columbium System with Collimator 4 Inches Long

Θ. Bragg angle for diffraction from NaCl crystal
***A*. Unresolved doublet of Ta$L\beta$ lines plus second-order Cb$K\beta$ line**
***B*. First-order Cb$K\alpha$ line**

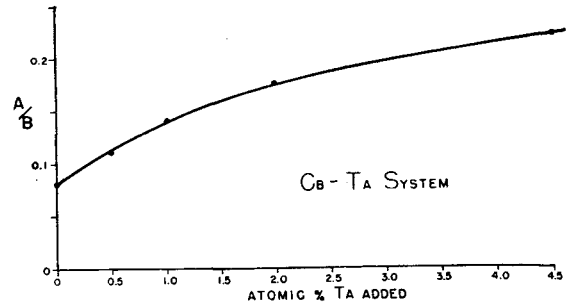

Figure 4. *A/B* Represents Ratio of Areas under Curves *A* and *B* from Spectra Such as Those in Figure 3

Ratio plotted against atomic per cent Ta added to Cb standard

counter. The general rule for determining the statistical accuracy of the Geiger counter data is that the standard deviation in counts is the square root of the total number of counts. The probable error is two thirds of the standard deviation. The areas used in calculating the ratios in Figure 4 were obtained by planimetering experimental curves such as those in Figure 3. To calculate the probable error in the data it was easier to add up the total counts obtained at 11 points on line A, Figure 3, and the total number of counts at 11 points on the background and treat these according to the usual method of handling Geiger counter data. The probable error in a line intensity measurement is given by

$$\text{P.E.} = {}^2/_3 (N_S + N_B)^{1/2} \qquad (1)$$

where N_S is the total number of counts of the line plus background and N_B is the total number of counts of the background. The relative probable error of the line above background measurement is then

$$\text{Relative P.E. } (N_S - N_B) = \frac{{}^2/_3 (N_S + N_B)^{1/2}}{N_S - N_B} \qquad (2)$$

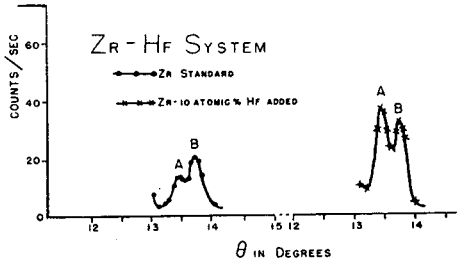

Figure 5. Representative Spectra of Hafnium-Zirconium System with Collimator 16 Inches Long

***A*. Hf$L\beta_2$ line. *B*. Unresolved Hf$L\beta_1$ plus second-order Zr$K\beta$ doublet. For a Zr standard with no Hf, *A* should not be present. Its appearance indicates that Zr standard contained some Hf impurity**

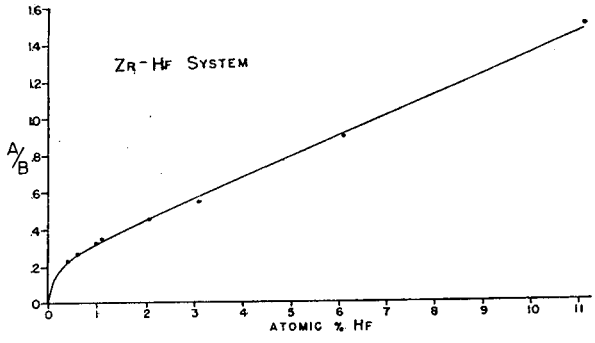

Figure 6. *A/B* Represents Ratio of Peak Intensities of Lines *A* and *B* from Data Such as Those in Figure 5 for Standard Specimens

Table I. Probable Error Data for Lines *A*, Figure 3, Using Equation 2

Atomic % Ta Added	Counts, N_S	Background Counts, N_B	Std. Dev. of N_S	Std. Dev. of N_B	Rel. P.E. of $N_S - N_B$, %
0	17,100	6200	131	79	0.93
0.5	22,700	7240	151	85	0.75
1	24,500	6540	157	81	0.65
2	27,050	6920	164	83	0.61
4.5	33,000	9040	181	95	0.57

In Table I for the tantalum-columbium specimens are listed the total number of counts, N_S, and the background count, N_B, the standard deviation in each of these values, and finally the relative probable error from Equation 2.

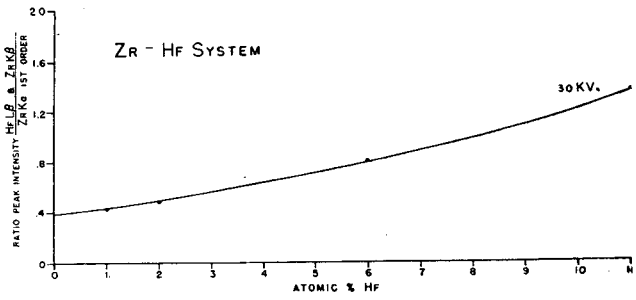

Figure 7. Ratio of Peak Intensities of Unresolved Hf$L\beta$ Plus Second-Order Zr$K\beta$ Doublet and Zr$K\alpha$ Line with Collimator 4 Inches Long

Tube voltage decreased to 30 kv. to reduce Zr spectrum preferentially

HAFNIUM-ZIRCONIUM SYSTEM

Method A was tried for the hafnium-zirconium system. The Hf$L\beta_2$ line was resolved from the Zr$K\beta$ plus Hf$L\beta_1$ doublet by using a collimator 16 inches long with nickel tubes $^1/_{16}$ inch in diameter. Samples were prepared for the calibration curve from three specimens of zirconium with known hafnium content loaned by the Bureau of Mines, Albany, Ore., and from C.P. zirconium oxide (from the Fansteel Products Company, North Chicago, Ill., listed as C.P. ZrO_2) with known hafnium content to which hafnium metal (Varlacoid Chemical Company, New York, N. Y., listed as 98–99% pure Hf) was added. The metallic zirconium obtained from the Bureau of Mines was converted to the oxide chemically to make all the samples as nearly alike as possible.

Figure 5 shows the spectra for the C.P. zirconium oxide (hafnium content 1.1 atomic %) and the mixture of C.P. zirconium oxide with 10 atomic % of hafnium added. The ratio of peak intensities A/B is plotted for the various samples in Figure 6. Because peak intensity A represents the amount of hafnium present, the curve should pass through the origin. Figure 6 is the calibration curve for the hafnium-zirconium system and is independent of the compounds in which they are present, just as for the tantalum-columbium system.

Data were also obtained on the hafnium-zirconium system by Method C, that is, lowering the x-ray tube voltage to reduce the intensity of the zirconium K spectrum relative to the intensity of the hafnium L spectrum. It was found impractical to reduce the voltage below 30 kv. because of the decrease in intensity of the hafnium lines. However, at 30 kv. the intensity of the zirconium spectrum was reduced preferentially and the results shown in Figure 7 were obtained. The ordinate represents the ratio of the peak intensity of the unresolved doublet of Hf$L\beta$ plus second-order Zr$K\beta$ to the peak intensity of the first-order Zr$K\alpha$ line. Either Method A or C seems to be satisfactory for hafnium-zirconium with approximately the same accuracy.

CONCLUSIONS

Any of Methods A, B, or C could be applied to the hafnium-zirconium system, but in the tantalum-columbium system it was not possible even with the 16-inch-long collimator to resolve the Ta$L\beta_2$ line from the Cb$K\beta$ second-order line. Therefore, only Methods B and C were applicable to tantalum-columbium. The accuracy of any of the methods depends on the intensity of the spectral lines—i.e., on the counting rate as measured by the Geiger counter and the Geiger counter statistics rather than experimental limitation. Greater accuracy is obtained by determining the integrated intensity of the lines than by merely determining the peak intensity when the lines are not bell-shaped.

Once the relation of area to peak intensity had been established, greater accuracy would be obtained by counting for the full time at the peak of the line.

In the tantalum-columbium system, the Ta$L\beta$ plus Cb$K\beta$ doublet was determined by counting for 32 seconds at each of 11 points on the line and 11 points on the background. From Table I for the 0.5 atomic % tantalum specimen, the relative probable error was 0.75%. The probable error in the area under the Cb$K\alpha$ line was negligibly small compared to this. Therefore, the probable error in ratio A/B was about 1%. In Figure 4, at 0.5 % tantalum, ratio A/B was about 0.11. The probable error was 1% of this or 0.001. From the curve, it is seen that ratio A/B changes by 0.06 in going from 0 to 1% tantalum. Therefore, 0.001 represents 0.02% tantalum. The measured value for the tantalum content in this region has a statistical fluctuation of 0.02/0.5 or 4% of the amount present.

In the hafnium-zirconium system, the accuracy was not as great by Method A because of the lower counting rate with the long collimator. For the zirconium standard, the accuracy was between 5 and 10% of the amount present for counting times of 32 seconds. However, Method B should give the same accuracy for hafnium-zirconium as it did for tantalum-columbium.

The limit of the minimum amount of hafnium or tantalum detectable would depend on the length of the counting time, but considering the data above would probably be of the order of 0.1% for reasonable counting times.

ACKNOWLEDGMENT

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Phenoldisulfonic Acid Method of Determining Nitrate in Water

Photometric Study

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Optimum conditions for nitrate analysis include absence of chloride ion and presence of a neutral or slightly alkaline medium during sample evaporation. Reproducible noninterference is possible at nitrite nitrogen levels below 0.2 p.p.m. All reagent volumes must be equalized in both visual colorimetric standards and samples. In many cases use of ammonium hydroxide for color development obviates necessity for final filtration.

FOR many years, nitrate determination has been difficult in this laboratory. Scrupulous adherence to the standard procedure (*1*) yielded an off-color yellow which taxed the imagination when compared against standards prepared in the accepted manner. At first, it was thought that the fault lay in the synthesis of the phenoldisulfonic acid, and extreme care was exercised in preparation of the reagent. This precaution failed to improve the situation in any material way.

A search of the literature revealed the Detroit difficulty to be no isolated case. Burke's recommendation (*3*) that 1 ml. of phenoldisulfonic acid be added to the standards was found to produce a better match between the standards and sample.

However, the bulk of the studies (*4–7*) to date have centered on the nitrate range above 1.0 p.p.m. A thorough photometric investigation of the nitrate reaction disclosed that factors which could be overlooked in the higher nitrate ranges must be controlled very carefully in the lower ranges; doubly so, because phenoldisulfonic acid is one of the few reagents available for the determinations of the relatively small nitrate concentrations present in many municipal water supplies.

Several improvements suggested themselves during this period of trouble-shooting. It was found that the success of the visual determination depends on the equalization of all reagent volumes in standards and samples alike, and that significant nitrate losses arise from the presence of chloride ion and the neutralization of the total alkalinity. Accordingly, a procedure embodying these findings was developed.

PHENOLDISULFONIC ACID REAGENT

The color of the phenoldisulfonic acid reagent depends on the initial color of the solid phenol and the acids used in the preparation. The whiter the crystals and solutions, the clearer and paler is the final reagent.

Oftentimes, the reagent possesses a faint color and reacts with strong alkalies to give a characteristic hue. This positive interference can be compensated for by the addition of identical volumes of reagent to samples and standards. This precaution nullifies the considerable error which may otherwise occur at the lower nitrate levels (under 0.5 p.p.m.), and also improves the visual color match where Nessler standards must be employed.

The practice of introducing equal volumes of all reagents into the blank and the visual and calibration standards is supported by the spectral transmittance curve obtained with a Beckman Model DU spectrophotometer. At wave length 410 mμ, the point of maximum absorption, the reagent blank records a

Table I. Effect of Alkalinity Neutralization on Nitrate Recovery from Synthetic Solutions

Nitrate Nitrogen Added	Total Alkalinity Added[a]	Nitrate Nitrogen Found		Loss Resulting from Neutralization
		Unneutralized sample	Neutralized sample	
P.p.m.	*P.p.m.*	*P.p.m.*	*P.p.m.*	%
0.50	100	0.50	0.21	58
0.50	250	0.51	0.16	68
0.50	500	0.48	0.11	77
0.25	100	0.26	0.09	64
0.50	100	0.50	0.18	64
1.00	100	0.99	0.53	47
2.00	100	1.97	1.59	21
0.25	100[b]	0.25	0.22	15
0.50	100[b]	0.51	0.44	12
1.00	100[b]	0.99	0.93	7
2.00	100[b]	1.99	1.90	5

[a] Total alkalinity expressed as $CaCO_3$. All alkalinities produced with Na_2CO_3.
[b] These alkalinities included 35 p.p.m. calcium as $CaSO_4$ and 10 p.p.m. magnesium as $MgSO_4$.

measurable transmittancy when compared against distilled water in a 10-cm. cell path. The same effect is registered at a 1-cm. cell depth, but to a lesser extent.

COLOR DEVELOPMENT

The fundamental reaction of the analysis is the nitration of phenoldisulfonic acid in an anhydrous medium. Color development results from the conversion of the acid nitration product to the alkaline salt. For this reason, the color may be read immediately upon development. Visual standards prepared from high grade reagents are stable for at least a month. Occasionally, slight color develops after several hours' standing, owing to side reactions between reagent and alkali. This belated development is characteristic of reagent solutions containing considerable initial color. In this event, fresh preparation of visual Nessler standards is advisable.

The chromatic system is such that nitrate nitrogen can be determined accurately at a wave length of 410 mμ in the range from 0.01 to 2.0 p.p.m. with a 1-cm. cell. Conformity to Beer's law also extends to the higher wave lengths of 470 and 480 mμ, enabling measurements with the Beckman spectrophotometer up to 12 p.p.m. nitrogen.

NITRATE LOSS CAUSED BY ACIDIFICATION

A thorough investigation of the current standard procedure disclosed that an appreciable reduction of nitrate resulted from acidifying the total alkalinity of the sample. The loss averaged slightly more than 10% in natural waters, and exceeded that value in solutions corresponding to zeolite-softened effluents, where the alkalinity is predominantly due to sodium bicarbonate.

The results reported in Table I show that the nitrate loss in distilled water rises with an increase in neutralized sodium carbonate alkalinity, ranging from 58% at 100 p.p.m. neutralized total alkalinity to 77% at 500 p.p.m. neutralized total alkalinity. Table I also reveals the nitrate loss at various steps when the neutralized sodium carbonate alkalinity is held constant at 100 p.p.m. All alkalinity values are expressed in terms of calcium carbonate. On a percentage basis the neutralization loss reaches a maximum at low nitrate concentrations and declines with increasing nitrate content.

Except for zeolite-softened effluents, perhaps, natural waters boast a more diversified mineral composition than that represented by a dilute sodium carbonate solution. Accordingly, synthetic solutions containing 35 p.p.m. of calcium ion added as calcium sulfate, 10 p.p.m. of magnesium ion added as magnesium sulfate, and 100 p.p.m. of sodium carbonate alkalinity were prepared and the loss resulting upon neutralization was noted at various nitrate nitrogen strengths. Table I shows the per cent loss to be considerably less than that occasioned in solutions composed of neutralized sodium carbonate alone, but on a level with that occurring in natural waters, as demonstrated in Table III. Thus, the mixed mineral salts present in a natural water reduce but fail to prevent entirely nitrate losses attendant upon the addition of dilute sulfuric acid. It is probable that neutralization of the sample to a pH below 5.0 introduces sufficient acid to release some nitric acid which might be volatilized during evaporation. As in the case of the neutralized sodium carbonate alone, the neutralization loss reaches a maximum at low nitrate strengths and declines with increasing nitrate concentration.

Although no acid natural waters were available for investigation, these findings suggest the advisability of raising the sample pH to the neutral or slightly alkaline region before evaporation is undertaken. Because most natural supplies are initially of a mildly alkaline reaction, such a step would be limited to a relatively few untreated samples.

EFFECT OF CHLORIDE ON NITRATE RECOVERY

Small amounts of chloride ion cause substantial reductions in the nitrate values of synthetic solutions. Table II reveals the extent of these losses in distilled water dosed with chloride ion. As little as 5 p.p.m. of chloride produce a 12% decrease in nitrate recovery, while higher chloride values cause correspondingly greater losses.

Table II. Effect of Chloride on Recovery of 0.5 P.P.M. of Nitrate Nitrogen from Synthetic Solutions

Chloride Added	Nitrate Nitrogen Recovery	Loss Resulting from Chloride	Nitrate Nitrogen Recovery after Chloride Removal
P.p.m.	*P.p.m.*	%	*P.p.m.*
0	0.50	0	0.50
5	0.44	12	0.49
10	0.40	20	0.50
25	0.35	30	0.51
50	0.33	34	0.51

These losses probably originate from the interaction of the hydrochloric and nitric acids liberated by the strongly acidic phenoldisulfonic acid reagent. For this reason, a minimum of chloride can be tolerated. Because most water supplies contain some chloride ion, it is important that the concentration be ascertained and the ion removed by the addition of standard silver sulfate solution before analysis is undertaken.

The application of silver ion invariably results in minute quantities of silver remaining in the solution finally made alkaline to develop the characteristic nitrate color. Alkalies such as sodium and potassium hydroxides peptize small amounts of silver hydroxide, imparting an off-color brownish hue to the solution and thereby making color matching difficult. Ammonium hydroxide, on the other hand, complexes the silver ion and enables an excellent visual match between color standards and samples. Another advantage of ammonium hydroxide is that filtration is unnecessary in the case of waters low in magnesium and iron.

The chloride ion in some waters can be removed by merely adding the equivalent amount of standard silver sulfate solution and centrifuging immediately for 15 to 30 minutes. Other waters require heat to coagulate the silver chloride, followed by filtration for best results. The Flat Rock samples, reported in Table III, were subjected to such treatment in order to precipitate all of the colloidal silver chloride and obtain a final yellow color which would visually match the Nessler standards.

Table III. Analysis of Natural Waters

Sample Source	Total Alkalinity Content[a]	Chloride Content	Nitrate Nitrogen Found in Untreated Sample	Nitrate Nitrogen Found in Sample after Chloride Removal: Total alkalinity neutralized	Nitrate Nitrogen Found in Sample after Chloride Removal: Total alkalinity unneutralized
	P.p.m.	*P.p.m.*	*P.p.m.*	*P.p.m.*	*P.p.m.*
Flat Rock raw 1	180	10	0.93	0.94	1.02
Flat Rock raw 2	153	7	0.60	0.62	0.65
Ypsilanti Township well	235	21	0.17	0.20	0.23
Ypsilanti well	245	18	0.12	0.13	0.16
Ann Arbor	188	11	0.50	0.53	0.62
Ann Arbor well	190	10	0.11	0.11	0.12
Willow Run village wel	210	4	0.00	0.00	0.00
Detroit raw 1	79	7	0.12	0.14	0.17
Detroit tap 1	74	7	0.12	0.14	0.17
Detroit raw 2	79	8	0.12	0.15	0.19
Detroit tap 2	71	8	0.12	0.15	0.19
Detroit factory well	100	1000	0.00	0.68	0.77

[a] Total alkalinity expressed as $CaCO_3$.

NITRITE INTERFERENCE

By virtue of family resemblance and susceptibility to oxidation, considerable amounts of nitrite ion interfere with the nitrate determination. Concentrations below 0.2 p.p.m. of nitrite nitrogen exert no effect on the phenoldisulfonic acid reagent, but concentrations in excess of that amount yield erratic and unreproducible results. At 1.0 p.p.m. of nitrite nitrogen, the positive interference varied from 0.00 to 0.04 p.p.m. in terms of nitrate nitrogen; at 5.0 p.p.m., the amount of nitrate color developed varied from 0.04 to 0.75 p.p.m. No two runs gave identical or even closely similar values.

Because municipal supplies seldom contain 0.2 p.p.m. or more of nitrite nitrogen, interference from this quarter is not so general or serious as that deriving from the presence of chloride.

APPARATUS AND REAGENTS

Beckman Model DU spectrophotometer with 10.005-cm. and 1.001-cm. Corex cells.

Cenco-Sheard-Sanford Photelometer with blue filter near 410 mμ, and tubular cells with a 17-mm. light path (routine analysis).

Tall-form 100-ml. Nessler tubes for visual colorimetric investigations.

Phenoldisulfonic Acid Reagent. Dissolve 25 grams of C.P. phenol in 150 ml. of concentrated sulfuric acid, add 75 ml. of 15% fuming sulfuric acid, and heat for 2 hours on a hot water bath.

Stock Nitrate Solution. Dissolve 0.7216 gram of C.P. potassium nitrate in 1 liter of distilled water.

Standard Nitrate Solution. Evaporate 50.0 ml. of the stock nitrate solution to dryness on a water bath, dissolve the residue by rubbing with 2.0 ml. of phenoldisulfonic acid reagent, and dilute to 500 ml. with distilled water. The solution contains 10 p.p.m. of nitrate nitrogen. Prepare calibration curves and visual standards from this solution by taking the desired aliquots, adding 2.0 ml. of phenoldisulfonic acid reagent, and developing the color with ammonium hydroxide in accordance with the recommended procedure.

Standard Silver Sulfate Solution. Dissolve 4.397 grams of the C.P. salt in 1 liter of distilled water. One milliliter of this solution is equivalent to 1.0 mg. of chloride ion.

Concentrated ammonium hydroxide solution (density 0.90), C.P.

RECOMMENDED PROCEDURE

Determine the chloride content of the water (*2*) and treat 100 ml. of the sample with an equivalent amount of standard silver sulfate solution. Remove the precipitated chloride either by centrifugation or by filtration, coagulating the silver chloride by heat if necessary. Transfer the clarified sample to a casserole and evaporate to dryness over a hot water bath. Rub the residue thoroughly with 2.0 ml. of phenoldisulfonic acid reagent to ensure solution of all solids. If need be, heat mildly on the hot water bath a short time to dissolve the entire residue. Dilute with 20 ml. of distilled water and add concentrated ammonium hydroxide solution (about 6 to 7 ml.) until maximum color is developed. Filter any resulting flocculent hydroxides from the colored solution into a 100-ml. volumetric flask or Nessler tube, dilute to the mark, and mix thoroughly.

Make photometric readings in cells of appropriate light path (1-cm. cells are suitable) against a blank prepared from the same volumes of phenoldisulfonic acid reagent and ammonium hydroxide used in the determination. Measure transmittancy at a wave length of 410 mμ or in conjunction with a blue filter exhibiting maximum absorption in the range from 400 to 425 mμ.

Add 2.0 ml. of phenoldisulfonic acid reagent to all color standards if visual comparison is employed.

ANALYSIS OF NATURAL WATERS

The chloride content of the natural waters investigated in this study ranged from 4 to 1000 p.p.m. while the total alkalinity varied between 71 and 247 p.p.m. Three sets of parallel experiments were conducted on each sample. In the first set, the sample was evaporated over a boiling water bath without any pretreatment. In the other two sets the chloride was first precipitated with the required amount of standard silver sulfate solution; then the total alkalinity of one 100-ml. portion was neutralized with 0.02 *N* sulfuric acid and evaporated to dryness on a water bath, parallel with a second 100-ml. portion in which the alkalinity was left unneutralized.

Coincident with the findings obtained on the synthetic solutions, the maximum nitrate values for each natural water resulted in the samples from which the chloride was removed and the total alkalinity was left unneutralized. The lowest values occurred when the chloride was allowed to remain and the total alkalinity was neutralized. Slight improvement was noted when the sample was left untreated. Still greater improvement was evident when the chloride was eliminated but the neutralization was retained.

Only two of the waters, Detroit and Flat Rock, had measurable quantities of nitrite. The highest nitrite content of the Flat Rock samples was 0.04 p.p.m. of nitrogen, whereas both Detroit raw samples had 0.001 p.p.m. of nitrite nitrogen.

With the exception of the Detroit and Flat Rock supplies, which are of surface origin, all samples were drawn from ground water sources. All except Detroit water had a total alkalinity and hardness in excess of 100 p.p.m., as calcium carbonate.

DISCUSSION

The data suggest the advisability of retaining the alkalinity normally present in most natural supplies as a means of minimizing the nitrogen losses attendant upon the neutralization currently recommended in the phenoldisulfonic acid method of nitrate analysis. The need is also indicated for removing as much chloride ion as possible, because of a natural incompatibility with nitrate in the highly acid medium required for the dominant reaction. Studies on synthetic and natural samples corroborate the importance of the losses occurring at low nitrate concentrations in the absence of these precautionary steps. The method is accurate to ±0.01 p.p.m. on known nitrate concentrations in the region below 1.00 p.p.m. of nitrogen. An average reproducibility of 0.01 p.p.m. has been achieved on typical routine natural water samples in this laboratory.

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Flame Photometer Attachment as an Excitation Source for the Spectrograph

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The Beckman flame spectrophotometer attachment may be used as an excitation source for sodium, potassium, and lithium analyses in conjunction with usual spectrographic equipment. Its use with a Bausch & Lomb large Littrow spectrograph is described. Using Eastman Type I-N plates, good results were obtained for the determination of sodium and potassium in plant and animal substances. When using a slit width of 45 microns and an exposure time of 30 seconds, approximate minimum readable sensitivities were potassium 10 p.p.m., sodium 20 p.p.m., and lithium 20 p.p.m. With lithium as internal control, a series of 18 determinations of sodium gave a standard deviation of 1.44%. For 20 potassium determinations the standard deviation was 0.47%. Agreement with other methods of analysis is good. Excitation conditions affect sensitivity. Maximum sensitivity was attained using a gas pressure of 6 cm. of water and an air pressure of 25 pounds per square inch. Optimum oxygen pressure varied, being 30 inches of water for potassium and 40 for lithium and sodium.

INTEREST in flame excitation methods for spectrochemical analyses has been revived recently by the development and availability of instruments for this purpose in this country (*2–5*). These instruments, primarily designed for the determination of elements requiring low excitation energies, apparently are based on the methods originally developed by Lundegårdh (*10*) who, working with an air-acetylene flame, was able to obtain highly reproducible results, apparently through good control of excitation conditions. Equipment similar to that developed by Lundegårdh has not been readily available in this country. Cholak and Hubbard (*7*) have described equipment, patterned after that of Lundegårdh, which was constructed for them. Their evaluation of its usefulness and efficiency also indicates highly accurate results and reproducibility.

Some of the newer equipment is completely self-contained, using photoelectric cells and galvanometers to indicate the intensity of emission, after suitable isolation of the spectral region required for the element under consideration (*5*). The Beckman flame spectrophotometer attachment, however, includes only a burner and atomizer and their appropriate controls. It has been designed primarily as an attachment to the Beckman spectrophotometer, but because of its construction it may serve also as an excitation source for ordinary spectrographic equipment. It differs from the Lundegårdh flame, in that it uses oxygen and natural or bottled gas, rather than oxygen and acetylene.

This paper describes the use of the Beckman flame attachment as an excitation source for the spectrograph and presents data regarding the sensitivity, precision, and accuracy obtained in the determination of sodium and potassium in materials of plant and animal origin. A limited amount of data on the influence of extraneous elements on analytical results as applied to sodium and potassium analyses in these materials is also presented.

MATERIALS AND METHODS

The Beckman flame spectrophotometer attachment was used as an excitation source in conjunction with a Bausch & Lomb large Littrow spectrograph. The flame photometer used was the type which had the heated atomizer chamber. A concentric type atomizer also was used. The flame photometer was modified by replacing the mirror supplied with the instrument with a piece of stainless steel bent so as to focus the light partially on the spectrograph slit. A cylindrical quartz lens was mounted directly in front of the slit of the spectrograph to focus the rays further. The use of the lens and concave mirror increased the sensitivity of the spectrograph approximately 50%. The burner of the flame source was approximately 20 cm. (8 inches) from the slit. No undue heating of the optical system was observed. The excitation procedure was standardized with respect to exposure time (30 seconds) and slit width (45 microns).

Although higher sensitivity could be obtained with increased exposure time and increased slit width, this was not necessary for the work planned in this laboratory. Other arrangements could be used for other samples as desired. Slit width would, of course, be limited by the amount of resolution desired.

All samples were prepared for analysis by drying, followed by ashing in a muffle at 550° C. The ash was then taken up in a solution containing 100 p.p.m. of lithium in the form of lithium chloride, which served as an internal standard. Sufficient solution was added to place the final potassium concentration between 20 and 100 p.p.m. For sodium the ash was diluted with the internal standard solution to make the sodium concentration fall within the limits of 50 to 400 p.p.m. These ranges were found most satisfactory for the procedure as outlined in this paper. All spectrographic data reported in this paper were obtained using lithium as an internal standard.

Standard solutions for calibration purposes were made from reagent grade chlorides of potassium, lithium, and sodium. For potassium, five concentrations were used: 20, 40, 60, 80, and 100 p.p.m. For sodium the concentrations prepared contained 50, 100, 200, 300, and 400 p.p.m. Each of these solutions also contained 100 p.p.m. of lithium which served as the internal standard. Five standards were exposed on each plate.

Eastman Type I-N spectroscopic plates were used. They were developed in D-19 for 4 minutes at 68° F. Line intensities were measured with an ARL-Dietert densitometer.

Spectral lines employed for analytical and internal standard purposes were as follows: potassium 7664.9 and 7699.0 A., lithium 6707.8 A., sodium 5890 and 5895.9 A., and calcium 4226.7 A. Calcium, however, is not in the spectral region for which this type of spectroscopic plate is intended to be used.

EXPERIMENTAL

Effect of Excitation Variables. In order to determine optimum operating conditions it was necessary to study the effects of three variables: oxygen, gas, and air pressures. It was found advisable to use air pressure at its maximum; in this laboratory this was 25 pounds per square inch (17,600 kg. per sq. meter). The air pressure apparently is related to the quantity of sample atomized into the flame per unit time. Gas pressure (natural gas was used) also was held at its maximum of 6 cm. of water. This value also gave the greatest sensitivity.

Considerable difference in sensitivity occurred with changes in oxygen pressure, as can be observed by an inspection of Figure 1, where spectral line intensity is plotted against oxygen pressure.

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Table I. Results of Duplicate Determinations of Sodium and Potassium in Plant Materials

Sample	Sodium, % Trial 1	Trial 2	Mean	Deviation, %	Potassium, % Trial 1	Trial 2	Mean	Deviation, %
Silage 1	0.044	0.044	0.0440	0.00	0.98	0.98	0.980	0.00
Silage 3	0.054	0.056	0.0550	1.82	1.19	1.21	1.200	0.83
Alfalfa pellets	0.037	0.039	0.0380	2.64	2.17	2.14	2.155	0.70
Brome pellets	0.041	0.041	0.0410	0.00	2.36	2.38	2.370	0.42
Soybean pellets	0.025	0.025	0.0250	0.00	1.72	1.91	1.815	5.24
Soybean meal	0.012	0.016	0.0140	14.25	1.29	1.32	1.305	1.15
Wheat grass 1	0.068	0.074	0.0710	4.22	2.85	2.85	2.850	0.00
grass 2	0.110	0.115	0.1125	2.21	3.42	3.46	3.440	0.58
Oats grass 1	...	...	...	...	3.22	3.23	3.225	0.15
grass 2	...	...	...	...	2.80	2.73	2.765	1.26

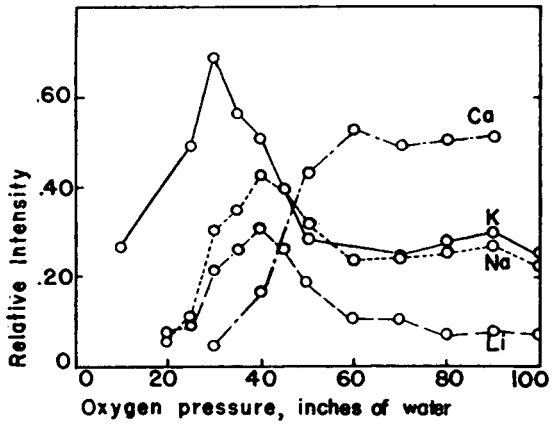

Figure 1. Effect of Oxygen Pressure on Relative Intensity of Potassium, Sodium, Lithium, and Calcium

A maximum value is obtained for each element, followed by a decrease. Maximum sensitivity is obtained for potassium at an oxygen pressure of 30 inches of water; for potassium and lithium the value is 40 and for calcium 60. These values roughly follow the order of ionization potentials of these elements. Because of these data a value of 40 inches of water was chosen as the best value for both potassium and sodium and was used for the data reported herein.

Table II. Precision of Spectrographic Determination of Sodium and Potassium

Element	No. of Determinations	Range, P.P.M.	Mean, P.P.M.	Standard Deviation, P.P.M.	Standard Deviation, %
Na	18	62–72	65.7	0.95	1.44
K	20	67–72	68.8	0.32	0.47

Using these conditions with an exposure time of 30 seconds and a slit width of 45 microns, the sensitivity of this method of excitation is as follows: potassium 10 p.p.m., sodium 20 p.p.m., lithium 20 p.p.m., and calcium 600 p.p.m. Standards used for lithium ranged from 10 to 100 p.p.m. and for calcium from 500 to 1000 p.p.m.

Precision of Method. Precision can be determined well from the results of duplicate determinations made for both potassium and sodium (Table I). Data are also presented in Table II on a series of 20 potassium and 18 sodium determinations made on the same sample. The standard deviation for potassium was 0.47%, and for sodium a value of 1.44% was obtained.

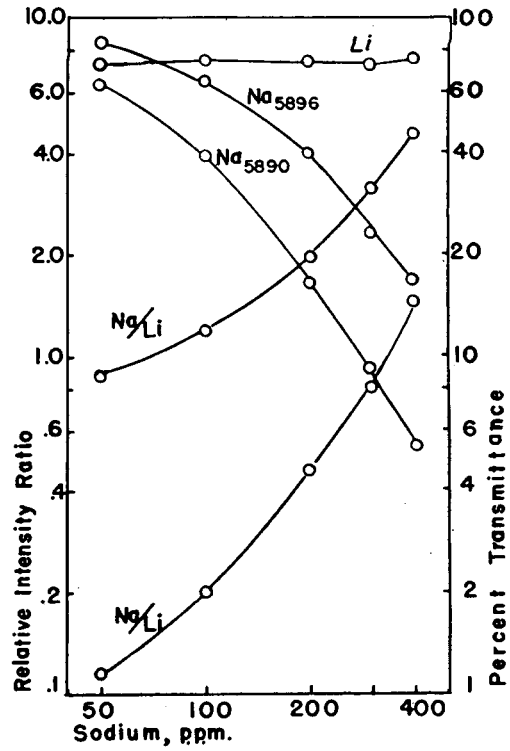

Figure 2. Typical Calibration Curves for Sodium in Plant and Animal Material

Calibration curves for potassium and sodium are given in Figures 2 and 3, with lithium as an internal standard and without internal control. The data are plotted by two methods; the lines sloping downward are plotted with reference to the per cent transmittance only and represent typical calibrations without the use of the internal standard. The lines sloping upward are relative intensity curves using lithium for internal control. The per cent transmittance of the lithium line is also plotted in Figure 2 in order to show graphically the reproducibility of the line intensity. The calibrations are not the usual straight lines obtained by other methods of excitation. This effect has been described as being due to cooling in the outer portions of the flame (*2*). Comparing the two calibrations given for sodium (see Figure 2), in which the two spectral lines show similar curvatures regardless of line intensity, shows that the effect is not due to operating on the nonlinear portion of the developing curve.

Effect of Extraneous Elements. Berry, Chappell, and Barnes (*5*) and Parks, Johnson, and Lykken (*11*) have reported the effects of certain extraneous substances on the intensity of emission of the spectral lines in the flame. A limited amount of similar data is presented in Figure 4, in regard to the effects of potassium, sodium, and lithium on each other. The range of values used covers those usually encountered in working with plant and animal materials. It is evident that within this limited range no general trend occurs. Such data, however, would not be necessarily valid outside the limits of this study.

Comparison with Other Methods. The spectrographic method has been compared with the more common chemical methods used for potassium and sodium. In Table III are presented data on potassium determinations. Only two samples were available that had been analyzed by the chloroplatinate procedure (*1*); the agreement on these two samples seems to be good. The remaining potassium determinations were made by means of the sodium cobaltinitrite reagent suggested by Peech and English (*12*). The technique used with this reagent was that developed by Wolf (*14*). These data are in relatively good agree-

ment, the mean difference between the methods being 4.1%. Duplicate determinations made spectrographically were in closer agreement than those made by the colorimetric method, indicating greater precision for the spectrographic procedure.

Numerous sodium determinations have been made on plant materials, but no comparison with other methods is available. A series of samples of bovine urine and blood serum has, however, been analyzed by chemical and spectrographic methods, with the results reported in Table IV. The chemical method used was that of Weinbach (*13*). These results are also in good agreement and serve to illustrate the type of results to be expected when using the flame spectrophotometer attachment as an excitation source in these spectrographic techniques.

DISCUSSION

The data presented indicate that it is possible to use the Beckman flame spectrophotometer attachment as an excitation source with the usual type of spectrographic equipment.

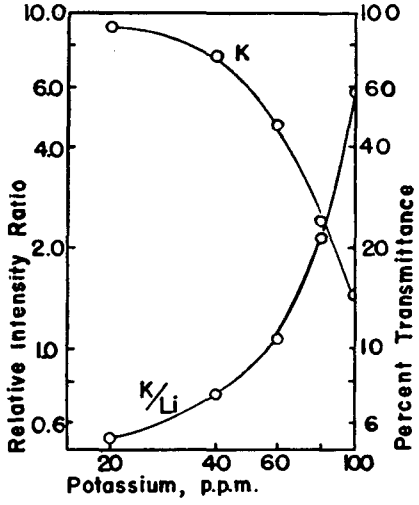

Figure 3. Typical Calibration Curves for Potassium in Plant and Animal Material

Table III. Comparison of Chemical and Spectrographic Methods for Determination of Potassium

Sample	Spectrographic K, %	Chemical K, %	Difference, %
Oat grass	3.23	3.34[a]	+3.3[a]
	2.77	3.04[a]	+8.9[a]
Wheat grass	2.16	2.27	+4.9
	2.44	2.65	+7.9
	2.96	3.23	+8.3
	2.72	2.78	+2.9
	2.50	2.70	+7.5
	2.02	1.90	−6.4
	1.92	1.90	−1.1
	1.93	2.11	+8.6

[a] Chloroplatinate procedure used on these two samples.

Table IV. Comparison of Chemical and Spectrographic Methods for Determination of Sodium

Sample		Spectrographic Na, P.P.M.	Chemical Na, P.P.M.	Difference, %
Bovine blood	2	3150	3660	+13.9
Serum	4	3200	3690	+13.2
	6	3350	3610	+ 7.2
	8	3300	3610	+ 8.6
	10	3450	3680	+ 6.3
	12	3450	3650	+ 5.5
Bovine urine	2	350	356	+ 1.7
	4	1160	1380	+15.9
	6	790	742	− 6.2
	8	100	96	− 4.0
	10	135	148	+ 8.8
	12	110	96	−12.7

The elements studied have included only potassium, lithium, sodium, and calcium. Data regarding calcium indicate that too low a sensitivity is obtained for use with most plant and animal materials without concentration of the calcium. The spectroscopic plates used, however, are not considered too sensitive in the region where the calcium lines are located (4226.7 A.). It is possible that some other type of plate, designed for this wave-length region, together with increased slit width and exposure time, would make calcium determinations possible with the flame excitation source.

The procedure has the advantage of simplicity, as compared with chemical methods usually used for the determination of sodium and potassium. The precision is also good, and compares favorably with other methods. Spectrographic determinations of sodium and potassium have, in general, been less precise than for many other elements—for example, Helz and Scribner (*9*) in reporting on minor elements in portland cement indicate a probable error of a single determination for sodium oxide to be 5%; for potassium oxide the error reported was 8%.

The original unheated atomizer chamber also was tested in this work. A gradual decrease in sensitivity occurred during a series of readings. This presumably was due to the cooling of the atomizer chamber as the sample evaporated, followed by recondensation of the vapor on the sides of the chamber. This fault seems to have been completely corrected by means of the heated jacket on the atomizer chamber.

It is essential that samples be completely free of solid particles. The atomizer can clog readily. This effect is, however, easily observable and can be corrected by blowing air back through the atomizer tip.

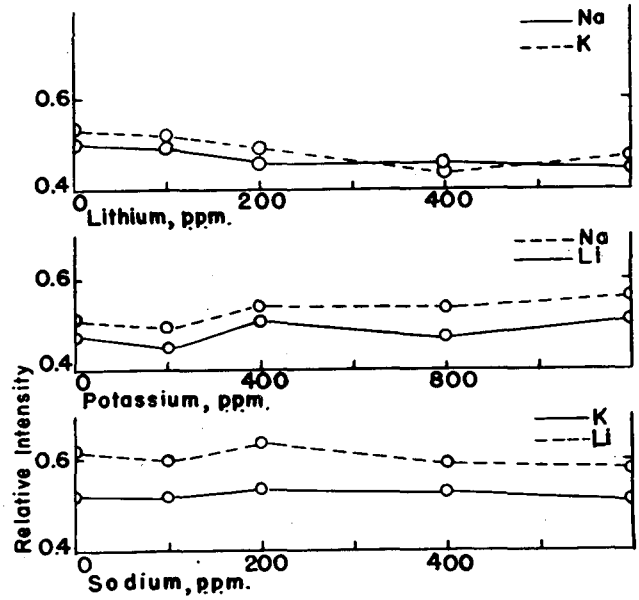

Figure 4. Effects of Varying Concentrations of Sodium, Potassium, and Lithium on Relative Intensity of Element Line

It has been found necessary to ash all samples containing organic substances prior to atomizing them into the flame. The organic materials have a tendency to clog the orifices of the burner, and this is followed by a loss in sensitivity. The ashing procedure eliminates this difficulty. The technique used converted the ash primarily to chlorides; as a result, chlorides were used in the preparation of standards whenever feasible.

In an earlier bulletin (*3*) it was suggested that the sample be

diluted with one part of isopropyl alcohol to four parts of sample. Effects due to viscosity changes have been indicated (*4*). The effects have not been studied in this laboratory but the use of the alcohol mixture has been continued and all data reported in this paper have been obtained, using the alcohol dilution technique.

Eastman I-N plates were the only type found satisfactory. Other plates, including Type I-L, did not have sufficient sensitivity in the spectral region used. The Type I-N, which has been designed for use in the infrared region of the spectrum (*8*), apparently decreases in sensitivity in the wave-length region between the sodium and potassium lines. This probably accounts for the differences in sensitivity observed for these two elements, which are not in accord with those reported for arc and spark spectra elsewhere (*6*).

Plate development seemed more critical with Type I-N plates than with others. This was partly due to the relatively high gamma (2.65 at 7699.0 A.) produced by the plates and the developer used. These factors also account in part for the precision achieved in these determinations, as well as the narrow range of concentrations for which the method is suitable.

The procedure as described and evaluated appears to be a promising method for the determination of sodium and potassium in several types of samples. Accuracy and sensitivity are good, small samples are sufficient (2 to 5 ml.), and existing equipment in many laboratories may be utilized. Further study should lead to applications of the procedure to other types of samples and possibly to the determination of other metals which may respond sufficiently to this form of excitation.

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Mineral Analysis of Biological Material by Flame Spectroscopy

Apparatus and Application

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The construction is described of an inexpensive, simple burner with an all-plastic atomizer and glass chamber similar to those described by Griggs (*5*). With the use of a Bausch & Lomb medium quartz spectrograph 15 elements can be determined directly or upon the dissolved ash of biological materials with an accuracy of ±5%.

LUNDEGÅRDH (*6*, *7*) in Sweden published in 1929 a text on the use of a flame as the excitation source for spectral identification and quantitative determination of alkalies, alkaline earths, and a number of other elements. However, in 1941 the flame technique was being used by only two or three workers in the United States (*3*, *5*). Since 1944 many modifications of the flame-producing burner necessary for this method of analysis have been described in the literature and several are available through commercial instrument channels. After extensive experimentation the authors have devised a simple, inexpensive burner with which satisfactory results can be obtained from analyses of biological materials for certain minerals.

BURNER

The materials used in constructing the burner shown in Figure 1 are considerably less expensive than those employed in earlier burners.

The tip is a standard stainless steel product (Jarrell-Ash Company), specially rhodium plated, and is connected to the borosilicate glass tube with a rubber sleeve. The acetylene inlet is a piece of thick-walled capillary tube, sealed into the burner with Plicene.

Used with a Bausch & Lomb medium quartz spectrograph, the burner is mounted with the tip 4 cm. from the spectrographic slit. A flat, stainless steel mirror is mounted directly behind the flame, across the optical path of the spectrograph, to intensify the emission.

BURNER OPERATION

The burner is operated with compressed air supplied at a pressure of 30 pounds and acetylene from a tank at a water gage pressure of 23 cm. Both air and acetylene are water-saturated before entering the burner. An all-plastic atomizer (Jarrell-Ash Company) and glass atomizer chamber similar to those described by Griggs (*5*), except that the chamber and burner are connected by a standard-taper ground joint, are employed to introduce the sample. The atomizing unit and burner are easily cleaned after use. Wetting agents are not required in the operation of the burner and a screen below the burner tip, used in the Lundegårdh and later modifications, is unnecessary.

SPECTROGRAPHIC TECHNIQUE

In analysis for alkali metals the region 1 cm. above the blue cone of the flame is used, the region Lundegårdh designates as most

Table I. Spectral Lines and Sensitivities

Line	Sensitivity, Mg./10 Ml.	Line	Sensitivity, Mg./10 Ml.
Ag 3281	0.05	Li 6708	0.001
Ba 5535.5	1.0	Mg 2852	0.05
Ca 4227	0.004	Mn 4031	0.003
Co 3527	0.01	Na 3302	0.11
Cr 3579	0.005	Na 5890	0.002
Cu 3247.5	0.005	Ni 3515	0.1
Fe 3850	0.05	Sr 4607	0.002
K 4044	0.08		

Table II. Analytical Ranges

Element	Internal Standard	Analytical Range, Mg./10 Ml.
Magnesium	Co 3405	0.06–0.6
Sodium	Co 3405	0.25–2.5
Calcium	Co 3873	0.02–0.12
Potassium	Co 3873	0.47–4.7
Manganese	Co 3873	0.01–0.3
Copper	Co 3405	0.02–0.6
Iron	Co 3873	0.06–0.6

sensitive for these elements. Two-minute exposures are satisfactory with Eastman emulsion 33 plates. Wratten Wainwright panchromatic plates are used to investigate the red range of the spectrum.

The spectral lines used for analysis and their sensitivities under the analytical conditions are listed in Table I. Cobalt is used as the internal standard, lines 3405 and 3874 being the control lines. Standard solutions are analyzed on each plate and standard curves are drawn for each element from each plate. The analytical ranges found for the elements are given in Table II.

Attempts are not made to calibrate the plate emulsions as suggested by Cholak (*1*), but exposure and developing times are rigidly controlled. Plates are processed with mechanical agitation throughout, immersed in Eastman D-19 developer for 3 minutes, in 5% acetic acid solution for 30 seconds, then in Eastman x-ray finisher and fixer. Line densities are measured with a Leeds & Northrup densitometer.

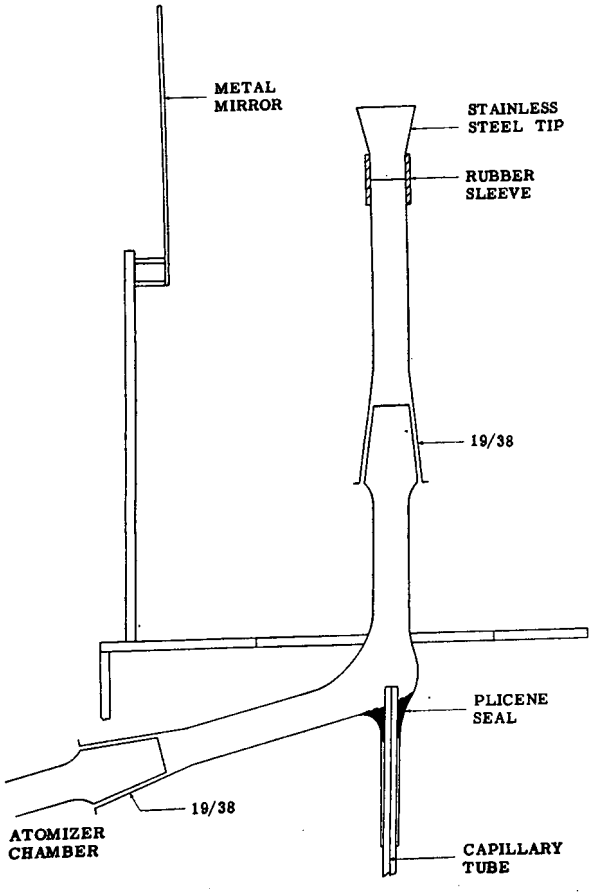

Figure 1. Burner for Flame Spectroscopy

APPLICATION OF METHOD

Using the flame spectroscopy technique described, quantitative analytical values have been obtained for sodium, potassium, magnesium, calcium, silver (*4*), copper, iron, strontium, and lithium in human and cow's milk, blood, urine, feces, and tissue. The method is satisfactory for analysis of the readily soluble ash from biological materials and, under the conditions described, provides reproducible results within an accuracy of 5%. For duplicate spectra, 3 ml. of solution are required. Sample material must be completely in solution and the total salt concentration must not be so high as to cause precipitation in the atomizer. As with other burners, the presence of strong oxidizing acids in final dilutions of ash must be avoided to prevent oxidation of the burner tip. The standard solutions for each sample must be prepared carefully to contain amounts of the elements to be determined consistent with the amounts known to be present in the sample. Background effects result when magnesium, iron, and aluminum concentrations vary widely.

Chemical methods of analysis are employed to check results of flame spectroscopy determinations: the gravimetric procedure (*11*) for calcium, the zinc uranyl acetate gravimetric method (*9*) for sodium, and the Peech (*8*) colorimetric procedure for magnesium. Results with spectrographic and chemical determinations check within the limits of error of both methods.

PREPARATION OF SAMPLES

Milk samples are dried from the frozen state with Desivac equipment. One gram of dry milk is reduced to white ash in a platinum crucible at 450° C. The ash is dissolved in, and diluted to 25 ml. with, 10% redistilled hydrochloric acid containing 0.75 mg. of cobalt per milliliter for determination of sodium, potassium, and magnesium. Calcium analysis requires additional dilution of 1 to 100 and adjustment of the cobalt concentration to 0.375 mg. per milliliter. Attempts to use fresh milk for the determinations with the internal standard are unsuccessful because precipitated protein clogs the atomizer.

Table III. Effect of Changing Concentrations on Results of Flame Analyses

(Values in milligrams per 10 ml.)

Solution[a]	Magnesium[b] A	Magnesium[b] B	Potassium A	Potassium B	Sodium A	Sodium B
Milk, diluted 1–10	0.159	0.162	2.3	2.2	0.33	0.40
Milk, diluted 2–10	0.290	0.296	4.4	4.2	0.74	0.84
Milk, diluted 1–10, 0.8 mg. K added	0.145	0.158	3.0	2.8	0.26	0.45
Milk, diluted 2–10, 0.4 mg. Na added	0.298	0.334	4.5	4.6	1.20	1.27
Milk, diluted 2–10, 0.2 mg. Mg added	...	...	4.7	4.8	0.90	0.88
Magnesium, 0.2 mg./10 ml.	0.20	0.21	...	...	...	...
0.4 mg./10 ml.	0.40	0.40	...	...	...	...
Potassium, 1.6 mg./10 ml.	...	...	1.7	1.6	...	...
Sodium, 2.0 mg./10 ml.	...	...	...	...	1.70	1.76
0.6 mg./10 ml.	...	...	...	...	0.37	0.54
1.5 mg./10 ml.	...	...	...	...	1.26	1.28

[a] All results obtained by reading against standard in which concentrations approximated those of milk and containing cobalt as internal standard.
[b] A, calculated from ratios of element to cobalt. B, calculated from ratios of (element minus background) to (cobalt minus background).

Samples of blood plasma, tissue, and feces were wet-ashed with nitric-perchloric acid mixture, evaporated to dryness, dissolved in, and diluted to correct concentration with 10% hydrochloric acid containing the proper concentration of cobalt. (Five milliliters of plasma provide sufficient material for magnesium, potassium, calcium, and sodium determinations.)

Samples of urine are diluted with the proper amounts of cobalt solution and the alkali metals are determined without ashing, but for other cations concentration of the urine is necessary.

Recovery experiments (Table III) were made with milk samples of different dilutions, milk samples of different dilutions to

which known amounts of elements to be determined had been added, and solutions of the elements only, to determine whether methods of calculation are justified or greater care of plate calibration is necessary. The results emphasize the necessity of considering background corrections in calculating final data from flame analysis spectrograms, especially with respect to sodium and magnesium. Recoveries with pure sodium solutions are not so complete as with sodium in diluted milk; this indicates that a standard is required which approximates the composition of the sample as shown by the values obtained with pure solutions of sodium in contrast to those obtained with dilute milk solutions.

The curves of ratio of element to cobalt and (element minus background) to (cobalt minus background) are drawn on semilog paper, the backgrounds being subtracted directly and not as recommended by Pierce and Nachtrieb (*10*). Plate calibrations using the two-line method of Churchill (*2*) were made, but the increase in accuracy does not warrant routine use of this procedure, despite the advantage of being able to read the concentrations of elements from straight-line calibration curves.

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Titration of Bases in Nonaqueous Solvents

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Organic bases may be accurately titrated in glacial acetic acid, benzene, chlorobenzene, nitrobenzene, chloroform, ethyl acetate, diethyl ether, petroleum ether, and acetonitrile, using methyl violet as the indicator. The titrant employed is a solution of perchloric acid in glacial acetic acid. Potentiometric titrations in most of the above solvents may be conveniently made with a pH meter using a glass–silver electrode combination without a salt bridge. Small amounts of water do not interfere, but larger amounts of water, alcohol, dioxane, and acetone should be absent.

IT WAS first pointed out by Conant (*3*) that the strength of basic compounds is much greater in glacial acetic acid than in aqueous solution. In this work curves were published for the potentiometric titration of a large number of bases with perchloric acid. Nadeau and Branchen (*6*) titrated amino acids in glacial acetic acid, using any one of several visual indicators to detect the end point. Blumrich and Bandel (*1*) determined several amines in acetic acid solvent, and Herd (*5*) applied this method to the determination of quinine. Small amounts of basic impurities in benzene (*8*) and in hydrocarbon oils (*9*) have been determined by first mixing acetic acid with the sample and then titrating with an acetic acid solution of perchloric acid. Palit (*7*) titrated certain bases in glycol–hydrocarbon solvent mixtures. It has recently been found (*4*) that many bases may be advantageously titrated in dioxane using a dioxane solution of perchloric acid as the titrant.

The purpose of this investigation is to demonstrate that both strong and weak bases may be conveniently titrated in benzene, chlorobenzene, nitrobenzene, chloroform, diethyl ether, ligroin (petroleum ether), and other relatively inert organic solvents. The titrant used is perchloric acid in either glacial acetic acid or acetic acid–chlorobenzene. Methyl violet serves as the indicator. In each case the end point is at least as sharp as when the base is titrated in glacial acetic acid. The chief advantage gained, however, is in the analysis of samples in which a base is dissolved in any of the above listed solvents. The determination of aniline in nitrobenzene, estimation of amines in hydrocarbon polymerization feed, and titration of bases extracted by chloroform from a mixture are but a few examples of practical applications. In each case the base may be titrated directly without first evaporating the solvent and redissolving in acetic acid.

PROCEDURE

A sample of suitable size is dissolved in 25 to 50 ml. of the chosen solvent. Two or three drops of methyl violet indicator (methyl violet in chlorobenzene) are added and the solution is titrated to a green color with 0.1 *N* perchloric acid in acetic acid.

The perchloric acid solution is prepared by dissolving 8.5 ml. of 70 to 72% perchloric acid in 1 liter of glacial acetic acid. If desired, the water may be removed by adding about 14 grams per liter of acetic anhydride, and allowing the solution to stand overnight. This solution is standardized against diphenylguanidine, prepared according to the directions of Carlton (*2*). Results obtained by this method agree with sodium carbonate standardization; diphenylguanidine is, however, preferred because it has a much higher equivalent weight and gives a somewhat sharper end point than sodium carbonate.

Data given in Table I indicate that the results obtained from titrating several representative bases in benzene, chlorobenzene, etc., are in agreement with those obtained from titration in glacial acetic acid.

INTERFERENCES

It is not possible to titrate bases in dioxane, alcohols, or acetone when perchloric acid in acetic acid is used as the titrant.

Even when other solvents are employed, dioxane and alcohol cause high results and a poor end point if present in much more than trace amounts. The presence of somewhat larger quantities of acetone can be tolerated.

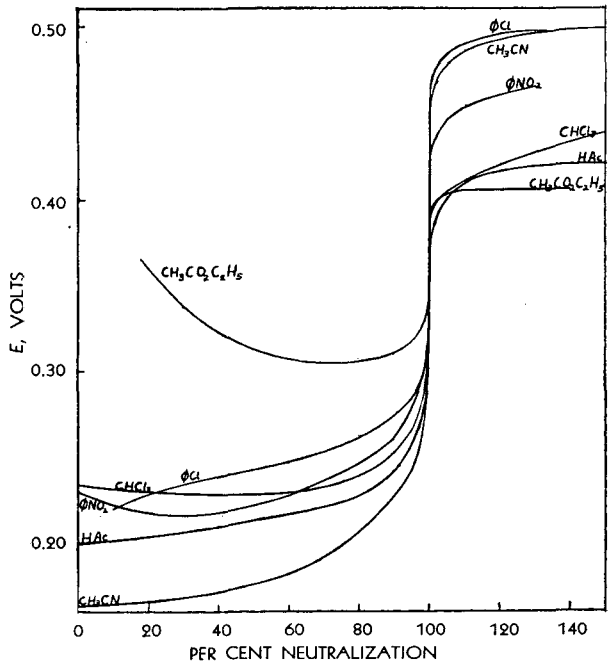

Figure 1. Potentiometric Titration of Aniline

The effect of water on titrations in glacial acetic acid was studied by adding varying amounts of water to acetic acid solutions of aniline. The aniline was then titrated with a perchloric acid solution made anhydrous by addition of acetic anhydride. The conclusion reached was that although larger amounts interfere, water in small amounts (up to about 3% of the original solvent) has little if any effect on either the sharpness of the end point or the accuracy of the titration. In view of this, it hardly seems necessary to add acetic anhydride to remove the last traces of water from the perchloric acid reagent.

POTENTIOMETRIC TITRATIONS

Potentiometric titrations were carried out using a Beckman Model G pH meter. A glass electrode was used as the indicator electrode and a silver wire with a thin coating of silver chloride served as the reference electrode. This electrode system possesses two distinct advantages over the chloranil-calomel electrode combination previously employed for titrations in glacial acetic acid. The glass electrode is inert to ordinary chemical attack and the use of the silver–silver chloride electrode eliminates a salt bridge.

It was found possible to titrate bases in acetic acid, chlorobenzene, nitrobenzene, ethyl acetate, chloroform, and acetonitrile by this method (Figure 1). Potentiometric titrations in benzene, ether, and petroleum ether failed. This failure is probably due at least in part to the very high resistance of the solution. In all cases equilibrium was rapidly attained. In these titrations methyl violet gave a sharp end point (violet → green or yellow) corresponding to the potentiometric end point.

There is but a single break in the potentiometric titration of brucine, despite the fact that brucine is a diacid base. A probable explanation is that in the above titration, slightly soluble brucine monoperchlorate is formed which prevents further reaction with the perchloric acid.

Table I. Titration of Bases in Nonaqueous Solvents with Perchloric Acid in Glacial Acetic Acid

Base	Solvent	Wt. Taken, Gram	$HClO_4$ Used, Ml.	Normality of $HClO_4$	Purity of Base, %
Pyridine	HAc	0.1357	17.07	0.0980	97.51
	Benzene	0.1375	17.30	0.0980	97.53
	Chlorobenzene	0.3243	41.03	0.0980	98.07
	Nitrobenzene	0.1615	20.35	0.0980	97.67
	$CHCl_3$	0.1915	24.04	0.0980	97.31
	Petroleum ether	0.1367	17.18	0.0980	97.42
Aniline	HAc	0.1755	18.52	0.1004	98.67
		0.1901	20.08	0.1004	98.76
	Benzene	0.2203	23.75	0.0985	98.87
		0.1984	21.36	0.0985	98.74
	Chlorobenzene	0.1414	15.23	0.0985	98.78
		0.2384	25.58	0.0985	98.40
	Nitrobenzene	0.2218	23.88	0.0985	98.74
		0.1720	18.52	0.0985	98.75
	$CHCl_3$	0.2660	28.60	0.0985	98.61
		0.0810	8.74	0.0985	98.95
	Ether	0.2150	23.14	0.0985	98.70
		0.1666	17.92	0.0985	98.65
	Ethyl acetate	0.1821	19.60	0.0985	98.71
		0.1892	20.40	0.0985	98.88
	CH_3CN	0.2016	21.69	0.0985	98.70
		0.1897	20.43	0.0985	98.77
Benzyl-amine	HAc	0.2012	18.97	0.0979	98.89
	Benzene	0.1679	15.81	0.0979	98.76
		0.2662	25.18	0.0979	99.22
	Chlorobenzene	0.2301	21.68	0.0979	98.83
		0.2517	23.74	0.0979	98.93
Brucine	HAc	0.6723	17.06	0.1001	100.2
	Chlorobenzene	0.6070	15.41	0.1001	100.2

DISCUSSION

In the titration of aniline, the end point in acetic acid is less sharp than in most other solvents. A particularly good end point is obtained in chlorobenzene and acetonitrile (see Figure 1). These solvents are therefore preferred to acetic acid for titrating bases.

The question of how strong a base must be in order to give a satisfactory methyl violet end point is important. Extremely weak bases may be titrated fairly accurately if an insoluble perchlorate salt is formed to assist in forcing the reaction to completion. Caffeine ($K = 4.1 \times 10^{-14}$), which forms an insoluble perchlorate, gives a fairly good separate end point; urea ($K = 1.5 \times 10^{-14}$), which forms no insoluble perchlorate in acetic acid, does not give a satisfactory end point. In general, basic nitrogen heterocyclic compounds tend to form perchlorates which are insoluble in most of the above solvents, while ordinary amines do not. It appears that the ionization constant (in water) of amines must be about 10^{-13} or greater for accurate titration to the methyl violet end point.

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RECEIVED February 15, 1950.

CORRECTION Attention has been called to an error in the title appearing in connection with a contribution by H. I. Feinstein [ANAL. CHEM., 22, 723 (1950)]. This should read "Identification and Determination of Nickel," not "microdetermination" as published.

Ultraviolet Spectrophotometric Determination of Molybdenum

GEORGE TELEP AND D. F. BOLTZ, *Wayne University, Detroit, Mich.*

A spectrophotometric study of the peroxymolybdic acid complex was made using a Beckman Model DU spectrophotometer. The effect of various variables on the maximum absorbancy was determined and optimum conditions were ascertained. Conformity to Beer's law was found for concentrations from 0 to 150 p.p.m. of molybdenum using 1.000-cm. quartz cells. The main interfering ions are iron, tungsten, vanadium, titanium, and fluorine. The recommended general procedure is rapid, accurate, and convenient.

THE colorimetric determination of molybdenum utilizing the peroxymolybdate complex in an alkaline solution was introduced by Funck in 1926 (*2*). This procedure had little significance, owing to the instability of the complex. Weissler utilized the peroxymolybdate complex in an acidic solution for the simultaneous spectrophotometric determination of molybdenum, titanium, and vanadium (*4*). Although a simultaneous determination of the three peroxide complexes was possible, little attention was given to the determination of molybdenum. Therefore, it seemed desirable to investigate critically the absorption spectra of the peroxymolybdic acid complex in the ultraviolet region of the spectrum. This study was made in order to ascertain the suitability of the pale yellow peroxymolybdic acid complex for an ultraviolet spectrophotometric determination of small amounts of molybdenum.

APPARATUS AND SOLUTIONS

The absorbancy measurements were made with a Beckman Model DU spectrophotometer and 1.000-cm. quartz cells. The spectrophotometer was equipped with an ultraviolet-sensitive phototube for high sensitivity in the 250 to 625 mμ region of the spectrum. The reference cell contained redistilled water for all the measurements.

A standard molybdate solution was prepared by dissolving 0.5000 gram of pure sodium molybdate in 1 liter of redistilled water containing 5 ml. of concentrated sulfuric acid. This solution was standardized by an A.S.T.M. procedure of analysis according to which silver molybdate is weighed (*1*). One milliliter of this solution contained 0.20 mg. of molybdenum. The perchloric acid solution used was 72% reagent grade. The hydrogen peroxide was 3% analytical reagent grade. Other acids used were C.P. reagent grade.

COLOR REACTION

The treatment of an acidic solution of molybdate ions with hydrogen peroxide results in the formation of the peroxymolybdic acid complex. This complex has a pale yellow hue with maximum absorbancy in the ultraviolet region.

In order to study the effect of certain variables on the maximum absorbancy, the following procedure was used.

A definite amount of the standard molybdate solution was transferred by means of a pipet to a 50-ml. volumetric flask. The desired amount of perchloric acid was added and the volume was adjusted to 50 ml. with redistilled water. After addition of 1 ml. of 3% hydrogen peroxide, the contents of the flask were thoroughly mixed and absorbancy measurements were taken from 250 to 450 mμ at 2-mμ intervals. The complexation is immediate, and the system is stable for at least 72 hours. In the study of the effect of diverse ions, a definite amount of the solution containing each ion was added before dilution and complexation.

EFFECT OF CONCENTRATION

Molybdenum Concentration. The absorption spectra for various concentrations of molybdenum was determined and conformity to Beer's law was found at 330 mμ in concentrations from 0 to 150 p.p.m. An intense absorption peak occurs at 330 mμ, as shown in Figure 1.

Acid Concentration. The effect of various concentrations of perchloric acid was determined using 100 p.p.m. of molybdenum and 1 ml. of hydrogen peroxide in a final volume of 50 ml. It was found that 1 to 15 ml. of perchloric acid had little effect upon the maximum absorbancy measured at 330 mμ. From this study, 5 to 10 ml. of perchloric acid per 50 ml. of solution were deemed to be a sufficient amount for attainment of maximum absorbancy. The study of the effect of other acids indicated that small concentrations of phosphoric acid have little effect, but other acids should not be substituted for perchloric acid in the procedure.

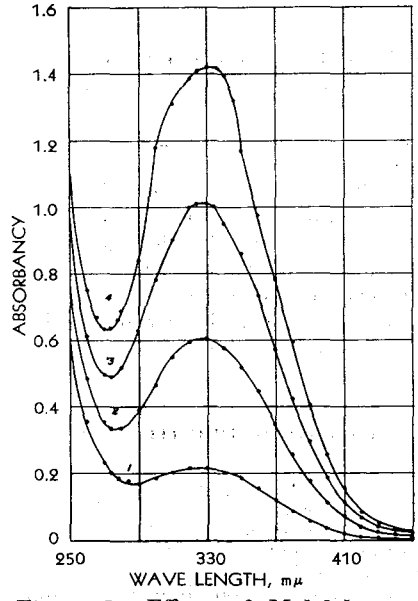

Figure 1. Effect of Molybdenum Concentration

1. 20 p.p.m.
2. 60 p.p.m.
3. 100 p.p.m.
4. 140 p.p.m.

Hydrogen Peroxide Concentration. The effect of various amounts of hydrogen peroxide was studied using 100 p.p.m. of molybdenum and 10 ml. of perchloric acid in a final volume of 50 ml. It was found that a minimum volume of 1 ml. of 3% hydrogen peroxide (per 50 ml. of solution) is necessary for attainment of maximum absorbancy.

Effect of Diverse Ions. The effect of various diverse ions was studied using 100 p.p.m. of molybdenum. Absorbancy readings were taken at 330 mμ in order to ascertain any changes in the maximum absorbancy. A negligible error was obtained with 1000

Table I. Interfering Diverse Ions

Ion	Added as	Amount Added, P.P.M.	Error, % of Desired Constituent	Permissible Amount, P.P.M.
Fe^{+++}	$Fe(ClO_4)_3$	100	60	10
WO_4^{--}	Na_2WO_4	100	4.5	40[a]
Ti^{++++}	$Ti(SO_4)_2$	100	25	20[b]
VO_3^-	NH_4VO_3	100	43	5
F^-	NaF	120	8.0	0

[a] In presence of citrate ions.
[b] In presence of phosphate ions.

p.p.m. of the following ions: aluminum, borate, calcium, cadmium, cobalt, cupric, bismuth, citrate, acetate, dichromate, magnesium, manganous, nickelous, plumbous, oxalate, malonate, stannate, silicate, sulfate, nitrate, tartrate, zinc, and zirconyl. Table I lists the interfering ions and their effect.

Fluoride Concentration. The effect of various amounts of fluoride was studied, using 100 p.p.m. of molybdenum. A negative error was caused by the fluoride ion. This precludes the advisability of attempting to remove the iron and titanium interference by use of fluoride ions.

INTERFERENCES

Tungsten Interference. The effect of various concentrations of tungsten was studied using 100 p.p.m. of molybdenum. It was found that 10 p.p.m. of tungsten gave an appreciable error. Wells and Grimaldi utilized citrate ions to lessen the tungsten interference in using the molybdenum thiocyanate colorimetric method (*5*). An investigation of the effectiveness of citrate ions in removing the tungsten interference when absorbancy is determined at 330 mμ revealed that up to 40 p.p.m. of tungsten could be tolerated in the presence of 1600 p.p.m. of citrate ions.

Iron Interference. The use of phosphate and tartrate ions to remove the iron interference by complexation was studied. A maximum concentration of 8 p.p.m. of ferric ion was successfully complexed using 5 ml. of phosphoric acid. A maximum concentration of 20 p.p.m. of ferric ion was complexed by 2200 p.p.m. of tartrate ions. Citrate ions had a complexing effect similar to that of the phosphate ions.

Interference of Titanium and Vanadium. Merwin studied methods of bleaching the titanium peroxide complex (*3*). Merwin's study indicated that phosphoric acid and citric acid reduce the intensity of the titanium peroxide color. The effect of various concentrations of titanium was studied using 10 p.p.m. of molybdenum and an acidic mixture of 5 ml. of perchloric and 5 ml. of phosphoric acids. A maximum concentration of 20 p.p.m. of titanium was successfully complexed. A maximum concentration of 15 p.p.m. of titanium can be complexed, using 1600 p.p.m. of citrate ions and 5 ml. of perchloric acid. There was no evidence that vanadium was complexed by these reagents. For larger amounts of titanium and for vanadium, corrections based on the absorbancies of the pure titanium and vanadium peroxy complexes can be made according to the method outlined by Weissler (*4*).

RECOMMENDED GENERAL PROCEDURE

Sample. Weigh, or measure by volume, a sample containing an amount of molybdenum such that the final solution contains not more than 0.20 mg. of molybdenum per ml. of solution. Acidify this solution with perchloric acid and dilute to a given volume.

Desired Constituent. Transfer a 25-ml. aliquot of this prepared solution to a 50-ml. volumetric flask and add 10 ml. of a 1 to 1 mixture of perchloric and phosphoric acids and sufficient water to bring the meniscus to the mark. Add 1 ml. of 3% hydrogen peroxide and mix thoroughly. Measure the absorbancy at 330 mμ in 1.000-cm. quartz cells.

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Determination of Levulose in Fruit

Polarographic Method

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A polarographic procedure for the determination of levulose in fruit is described. The sugars are extracted and prepared for measurement by conventional methods. The dextrose and sucrose present do not interfere and concentrations of levulose varying from 0.05 to 2.0 mg. per ml. are suitable for measurement. Ion exchange resins are used to control pH.

THE chemical methods for the determination of levulose are, in general, involved and time-consuming. In many of the procedures now in use it is necessary to determine the dextrose and levulose together as well as the levulose alone. An adjustment must then be made in the levulose value by the use of a factor and a series of approximations to compensate for the reducing power of the dextrose present. In some methods of analysis sucrose interferes and it must also be determined and a correction made. Because a direct determination of levulose, unhampered by dextrose or sucrose interference, is desirable, it seemed feasible to investigate the polarographic determination of this sugar.

Heyrovský and Smoleř (*4*) found that although aldehydes are reduced at the dropping mercury electrode, the aldoses (glucose, rhamnose, arabinose, mannose, galactose, lyxose) and disaccharides (maltose, lactose, sucrose) are not reduced. However, they found that ketoses (levulose and sorbose) give well defined polarographic waves. Kořínek and Babička (*7*) made analytical use of this reduction to follow the inversion of sucrose by the action of different bacteria. Heyrovský, Smoleř, and Šťastný (*5*) determined levulose in wine. Heyrovský (*3*) described its determination in the presence of sucrose and glucose in honey. Vavruch and Rubeš (*11*) determined levulose in candy. Wiesner (*12*) reported a polarographic investigation of the electroreduc-

tion of sugars, and Vavruch (*10*) the polarographic properties of levulose.

This paper outlines a procedure for the polarographic determination of levulose in fruit.

APPARATUS AND REAGENTS

A Heyrovský Model XII polarograph manufactured by E. H. Sargent and Company was used to obtain the current-voltage curves. The capillary characteristics were determined at 25° C. with an open circuit, the electrode dipping in a 0.1 *M* solution of calcium chloride. The value of $m^{2/3}t^{-1/6}$ for the capillary was 1.73 $mg^{2/3}t^{-1/2}$ where $m = 1.66$ and $t = 3.57$.

For routine analysis a simple Heyrovský, Erlenmeyer-style (15-ml.) cell employing a stationary mercury pool as the anode was used. An H-cell of the type described by Lingane and Laitinen (*8*) was used to determine the half-wave potential. For a 0.005 *M* levulose solution the half-wave potential *vs.* the saturated calomel electrode was found to be −1.7 volts, which is in agreement with values reported in the literature (*6*).

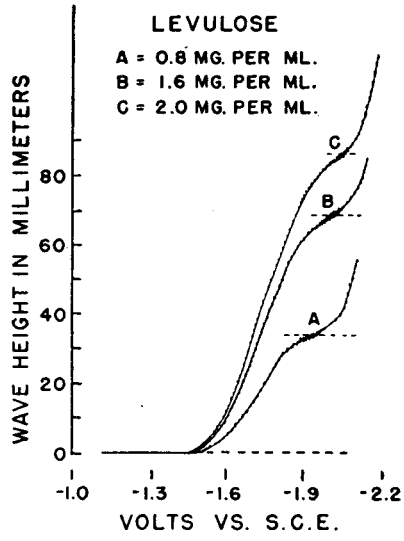

Figure 1. Representative Polarograms of Standard Levulose Solutions

Calcium chloride dihydrate, conforming with American Chemical Society specifications, was used as a supporting electrolyte as recommended by Vavruch (*11*). Gelatin was necessary to suppress the maxima. Cation-exchange resin Amberlite IR-100H-AG and acid-binding resin Amberlite IR-4B-AG were used in the control of pH, and D(−)levulose, made by the Pfanstiehl Chemical Corporation, was used without purification for the preparation of standard levulose solutions.

PROCEDURE

The sugars were extracted from the fresh fruits with 80% ethyl alcohol. Aliquots of the extract were evaporated on a steam bath to remove the alcohol. The residual water solution was filtered through Celite analytical filter-aid (*13*) and made to a final volume estimated to contain approximately 2 to 10 mg. of levulose per ml. Excess acid can be removed from this diluted solution by passing it through the Amberlite resins as previously described (*13*).

Aliquots, estimated to contain 40 to 100 mg. of levulose, were transferred to 50-ml. volumetric flasks, 5 ml. of 1 *M* calcium chloride dihydrate and 5 ml. of 0.2% gelatin were added, and the aliquots were made to volume with distilled water.

The polarographic cell was filled with the solution and the polarograms were made in the presence of air at room temperature (25° ± 1° C.), with current sensitivity, $R = 200$, and with a bridge voltage of 3. Three polarograms were made for each solution, the wave heights were measured in millimeters, and from the average wave height the concentration of levulose in milligrams per milliliter was read from a standard curve.

A standard curve was prepared from polarograms obtained from levulose solutions of known concentration, by plotting wave height in millimeters against concentration in milligrams per milliliter. The heights of the waves (see Figure 1) were measured by the third method described by Müller (*9*).

Table I. Ratio of Wave Height to Levulose Concentration

(Over range 0.8 to 2.0 mg. per ml.)

Levulose *Mg./Ml.*	Wave Height *Mm.*	Av. *Mm.*	Ratio *Mm./Mg.*
0.8	35.2, 35.4, 34.2, 34.3	34.8	43.5
1.0	45.0, 44.9, 44.2, 44.3, 44.6, 43.0	44.3	44.3
1.2	54.0, 52.0, 51.7	52.6	43.8
1.6	70.2, 70.2, 70.3, 70.5, 69.7	70.2	43.9
2.0	88.0, 88.4	88.2	44.1

Table II. Levulose Content of Fruits

Fruit	Polarographic %	Chemical %
Apple	6.67, 6.77, 6.50	6.72, 6.81
Grape, Thompson seedless	10.5, 10.8, 10.6	10.3, 10.7
Grapefruit	2.15, 2.22, 2.23	2.23, 2.23
Orange	2.11, 2.15, 2.11	2.13, 2.20
Peach	1.58, 1.55, 1.59, 1.56, 1.60, 1.61	1.83, 1.79
Pear	7.89, 7.89, 7.75	7.96, 8.16

RESULTS AND DISCUSSION

A standard curve was prepared from polarograms obtained for pure levulose solutions at intervals throughout the investigation. The data in Table I show a straight-line relationship. Polarograms were also made from solutions of levulose containing dextrose (National Bureau of Standards, standard sample 41) and sucrose (National Bureau of Standards, standard sample 17). The polarograms obtained for solutions containing levulose and dextrose in the ratio of 1 to 2 and for levulose and sucrose in the ratio 1 to 2 were the same as those obtained for pure levulose solutions of equal levulose concentration. Therefore, no corrections were needed for these sugars in any of the polarographic analyses in this report.

The results obtained by the chemical method (*1*) (Table II) were obtained on aliquots from the solution after the pretreatment had been completed for polarographic analysis. These direct comparisons show that the two methods gave values that were in good agreement.

A precipitate formed in the peach solution upon the addition of gelatin. The material causing the precipitation was not identified but was assumed to be tannin. The precipitant was removed by Baker and Adamson Code 1551 carbon, which does not adsorb significant amounts of levulose under the conditions that were used (*2*).

Polarograms obtained from the orange, grapefruit, and peach solutions without pH adjustment were badly distorted. When the pH was raised to 5.5 with 0.1 *N* sodium hydroxide, there was an appreciable residual current. However, normal polarograms were obtained when Amberlite resins were used to adjust the pH.

Some measurements of levulose were made by making polarograms of the fruit solutions prepared as directed and the same solutions plus a known added amount of levulose. The added height of the wave, due to the known amount of added levulose, was used to determine the ratio of height in millimeters to concentration of levulose in milligrams per milliliter. This method gave results comparable to those obtained by the standard curve; therefore, the wave height obtained for the treated fruit solutions could be compared directly with those obtained for pure levulose solutions to determine the levulose concentration.

Concentrations of levulose much lower than 0.8 mg. per ml. can be measured satisfactorily by varying the current sensitivity. The authors found that with $R = 20$ and with 0.01% gelatin present, concentrations of levulose from 0.05 to 0.25 mg. per ml. gave polarographic curves suitable for measurement. For concentrations from 0.15 to 0.60 mg. of levulose per ml. they used $R = 50$ and prepared the solutions with 0.015% gelatin.

The analytical results obtained at the various levulose concentrations were comparable—for example, in the analysis of grapes, values of 10.8, 11.1, and 10.6% were found with R = 20, R = 50, and R = 200, respectively.

Because the method is applicable over a wide range of concentration, 0.05 to 2.0 mg. per ml., it should be useful in a variety of problems involving levulose measurements in fruit.

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Colorimetric Determination of Panthenol and Pantothenates

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A rapid colorimetric method for the assay of panthenol and pantothenates is described, which can be applied for the assay of panthenol and D-calcium pantothenate in pure form as well as in tablets and ampoules. The results show good agreement with the microbiological method. An adaptation of the method deals with the determination of panthenol in multivitamin preparations. Through the use of an ion exchange resin column for the adsorption and elimination of interfering ionic substances the method is rendered specific for panthenol. The colorimetric method is based upon the formation of pantoyl lactone by hydrolytic cleavage in acid medium. The lactone reacts with hydroxylamine in the presence of alkali. The hydroxamic acid thus formed yields a purple color upon acidification in the presence of ferric chloride. This color, with a maximum absorption at 500 mμ, is utilized for photometric measurements. The effect of temperature, pH, and quantities of reagents added is described and data concerning the stability of the color developed are presented.

BECAUSE panthenol (α,γ-dihydroxy-β,β-dimethylbutyramide) and pantothenates assume considerable importance as members of the vitamin B complex family, a rapid chemical method for their determination was desired. A microbiological assay method for panthenol and pantothenates has been described by Walter (*10*, *11*). DeRitter and Rubin (*2*) modified this method for the determination of panthenol in the presence of pantoyl lactone and pantoic acid, and Drekter *et al.* (*3*) used excretion bioassays for their determination. Frost (*5*) assayed solutions of D-calcium pantothenate by means of their optical rotation and determined their stability under varied conditions. Crokaert (*1*) described a color reaction between β-alanine, one of the hydrolytic cleavage products of pantothenic acid, and 1,2-naphthoquinone-4-sodium sulfonate, while Szalkowski, Mader, and Frediani (*9*) reacted β-alanine with 2,4-dinitrophenylhydrazine and determined colorimetrically the precipitated hydrazone in pyridine. Hestrin (*6*) suggested that the color reaction for esters and lactones, described by Feigl *et al.* (*4*), might be utilized for a quantitative procedure. This reaction had previously been used by Lipmann and Tuttle (*7*) for the determination of acyl phosphates.

The method described is based upon Feigl's (*4*) color reaction after hydrolysis of panthenol or pantothenates to pantoyl lactone.

PRINCIPLE OF METHODS

Panthenol and pantothenates undergo hydrolytic cleavage in acid medium with the formation of pantoyl lactone and β-alanol and β-alanine, respectively. The pantoyl lactone reacts with hydroxylamine in alkaline solution to form the hydroxamic acid of pantoyl lactone. Upon acidification and addition of ferric chloride, a purple color complex is developed, which is utilized for photometric measurements (Figure 1).

Apparatus. A Klett-Summerson photoelectric colorimeter equipped with filter No. 50 and calibrated test tubes of 12.5-mm. diameter which accompany this instrument were used, but any type of instrument suitable for absorption measurements at a wave length of 500 mμ can be employed.

Reagents. Standard Solution. An aqueous solution of U.S.P. reference standard D-calcium pantothenate, dried in a vacuum desiccator over sulfuric acid for 24 hours, is prepared, containing 1.0 mg. of D-calcium pantothenate per ml.

The hydroxylamine–sodium hydroxide reagent is prepared by dissolving 7.5 grams of hydroxylamine hydrochloride in 100 ml. of 1 N sodium hydroxide (freshly prepared).

Sodium hydroxide, 1 N.

Hydrochloric acid, 1 N.

A 0.1% solution of 2,4 dinitrophenol in 95% ethyl alcohol.

Aqueous ferric chloride solution, 2%.

Procedure. To a sample aliquot of about 3 mg. of panthenol or pantothenates in 5 ml. of water, contained in a 50-ml. volumetric flask, 3 ml. of 1 N hydrochloric acid are added. The flask is capped loosely and the mixture is hydrolyzed by heating for 3 hours in an oven at 80° C. and then cooled to room temperature. Two milliliters of the hydroxylamine–sodium hydroxide reagent are added, followed by 5 ml. of 1 N sodium hydroxide. After 5 minutes' standing, 3 drops of 2,4-dinitrophenol indicator are added and the solution is carefully titrated with 1 N hydrochloric acid until a colorless end point is reached. The volume is then made up to 50 ml. with water.

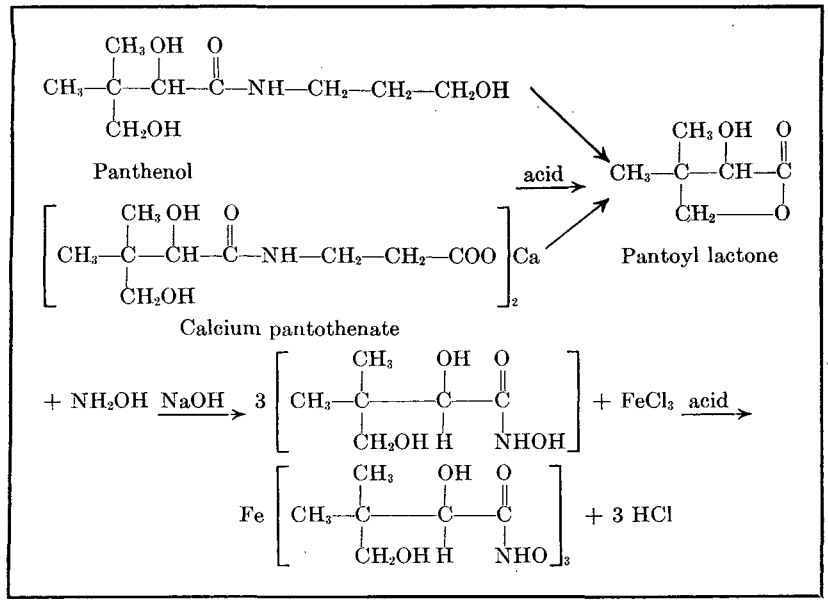

Figure 1

A 5-ml. aliquot is pipetted into a suitable colorimeter tube, followed by 1 ml. of 2% ferric chloride. The solution is mixed and the test tube gently tapped on the table top just prior to the colorimetric reading in order to eliminate interference due to bubble formation. Within 45 seconds to 1 minute after the addition of the ferric chloride reagent, the purple color developed is measured in the photoelectric colorimeter at 500 mμ and compared with a standard of similar concentration, prepared in the same manner from U.S.P. reference standard D-calcium pantothenate.

Prior to these measurements, the instrument is set at zero absorbance with water. Blanks for calcium pantothenate and panthenol are prepared by treating the same aliquots of the solution used in the determination in the same manner with omission of the hydrolysis in acid medium at 80° C., thus eliminating any preformed pantoyl lactone. The readings of these blanks are subtracted from the readings of the respective hydrolyzed solutions.

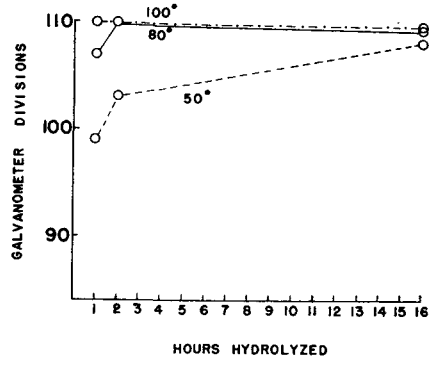

Figure 2. Effect of Temperature upon Acid Hydrolysis of Panthenol

Calculation of Results. If a solution containing panthenol is assayed against a standard solution of D-calcium pantothenate, the following formula may be applied:

$$\frac{A \times C \times D}{B \times E} = \text{mg. of panthenol per ml. of solution}$$

where

A = reading of hydrolyzed panthenol solution minus panthenol blank

B = reading of hydrolyzed D-calcium pantothenate standard minus calcium pantothenate blank

C = mg. of D-calcium pantothenate contained in B

$$D = \frac{\text{ml. wt. of panthenol} \times 2}{\text{mole. wt. of Ca pantothenate}} = \frac{205.13 \times 2}{476.33} = 0.8613$$

E = aliquot of panthenol solution used

DISCUSSION

The procedure described was arrived at after investigation of all factors which have a bearing upon the development of the color.

Effect of Temperature upon Acid Hydrolysis. The acid hydrolysis of panthenol and pantothenates, using 1 N hydrochloric acid, went to completion within 1 hour at 100° and within 2 hours at 80°, whereas at 50° complete hydrolysis occurred only after heating overnight (approximately 16 hours) (Figure 2). Because pantoyl lactone has a melting point of 92° and some decomposition might have been expected at higher temperature, hydrolysis at 80° C. for 3 hours was adopted in the procedure.

Effect of Varied Amounts of Hydroxylamine–Sodium Hydroxide Reagent. The effect of various concentrations of this reagent is shown in Figure 3. It is evident that maximum color intensity was obtained with 2 ml. of this reagent.

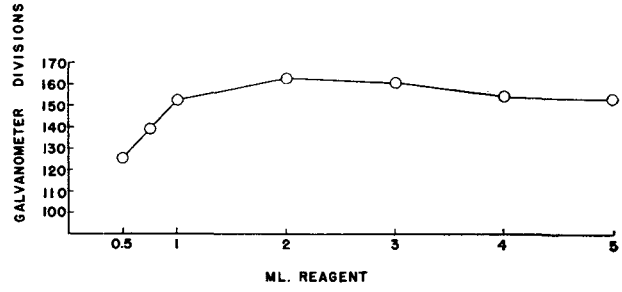

Figure 3. Effect of Varied Amounts of Hydroxylamine–Sodium Hydroxide Reagent

Effect of Temperature upon Formation of Hydroxamic Acid of Pantoyl Lactone. In alkaline medium pantoyl lactone is converted to pantoic acid, which produces no color under the conditions of the test. Increase in temperature will enhance the speed of this reaction. Because an alkaline medium is necessary for the formation of the hydroxamic acid of pantoyl lactone, some pantoic

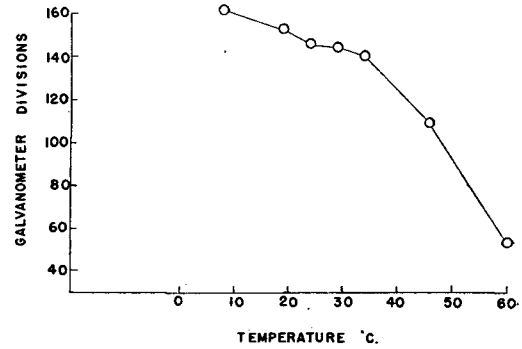

Figure 4. Effect of Temperature on Formation of Hydroxamic Acid of Pantoyl Lactone

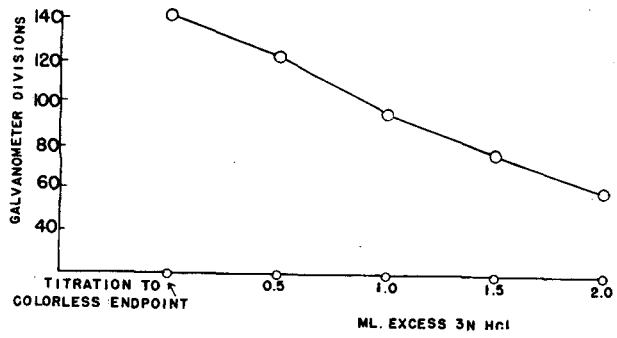

Figure 5. Effect of Excess 3 *N* Hydrochloric Acid

acid may be formed before complete conversion of the lactone to its hydroxamic acid. The effect of temperature upon the formation of the hydroxamic acid of pantoyl lactone is shown in Figure 4. Although immersion in an ice bath with a resulting solution temperature of 8° C. yielded maximum color intensity, a decrease in absorbance of 8% occurred at 20° C. Between 20° and 35° C. only minor losses in color intensity were observed, while higher temperatures caused considerable formation of pantoic acid with consequently low absorbance values. For best reproducibility, the reaction was carried out at room temperature, in view of the fact that a standard of about the same concentration as the sample is run simultaneously and thus is subjected to exactly the same conditions.

Effect of Excess Hydrochloric Acid. As the final color must be developed in acid medium, it was necessary to neutralize the sodium hydroxide and to obtain a definitely acid pH. A suitable indicator was found in 2,4-dinitrophenol, inasmuch as at the end point of the titration at a pH of 2.7 a colorless solution was obtained. When after titration to a colorless end point an excess of hydrochloric acid was added, a marked decrease in color intensity was observed (Figure 5).

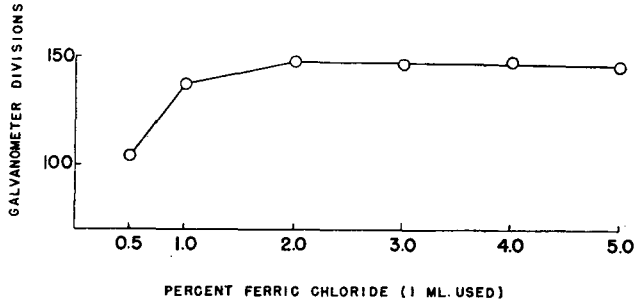

Figure 6. Effect of Excess Ferric Chloride

Experiments were conducted with the view of substituting buffer solutions for the titration. However, buffers tested, such as acetate, citrate, and hydrochloric acid–potassium chloride buffers, partially or completely inhibited the formation of the typical color. The time of standing after the titration and dilution to volume was found to be not critical in periods up to 1 hour.

Effect of Excess Ferric Chloride. In order to determine the effect of various quantities of ferric chloride, experiments were run, using 1 ml. of ferric chloride solution of various concentrations. As demonstrated in Figure 6, maximum absorbance was obtained with 1 ml. of 2% ferric chloride. Higher concentration did not increase the color intensity. In order to eliminate the error of a high blank, 1 ml. of a 2% ferric chloride solution was used.

Absorption Curve. An absorption curve of the color developed, using a solution of pure pantoyl lactone, showed a maximum at 500 mμ on a Beckman spectrophotometer, Model DU (Figure 7). Therefore filter No. 50 was used on the Klett-Summerson instrument.

Stability of Color Developed. Because the color rapidly reaches its maximum, remaining stable for 1 minute with gradual fading thereafter (Figure 8), readings were taken at between 45 seconds and 1 minute after addition of the ferric chloride reagent.

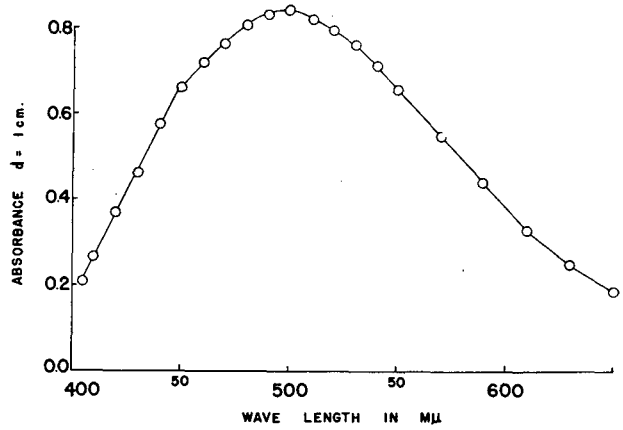

Figure 7. Absorption Curve of Color Developed
Pantoyl lactone, 180 γ per ml.

Calibration Curve. A plot of absorbance against concentration was found to be linear and passed through the origin. Beer's law was obeyed over the entire suitable range of concentration. With the Klett-Summerson instrument this range was held to the limits of 10 to 40 micrograms of pantoyl lactone per ml. of final solution.

RESULTS

Using the previously described method, samples of pure panthenol, calcium pantothenate, and pharmaceutical preparations such as tablets and ampoules containing panthenol were assayed. Panthenol is marketed exclusively in its D-form and for comparison dextrorotatory calcium pantothenate was used, as only the D-form is considered biologically fully active. The results were tabulated alongside those obtained by the microbiological method of DeRitter and Rubin (*2*) and an average deviation of 2.7% was found (Table I).

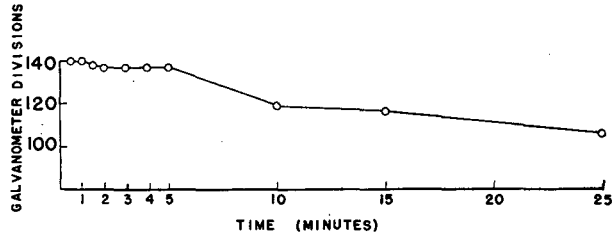

Figure 8. Stability of Color Developed

In liquid preparations some hydrolysis may occur with formation of pantoic acid or pantoyl lactone, depending upon the pH of the solution. Panthenol and pantothenates will hydrolyze to pantoic acid in alkaline medium, while acid hydrolysis will proceed to the lactone. Because the color due to any pantoyl lactone present will appear in the blank and thus is subtracted from the reading of the hydrolyzed sample, only preformed pantoic acid need be determined by microbiological procedure and subtracted from the results. Ten different assays on ampoules, run by this method, showed an average deviation of 2.7% from the microbiological method with a maximum deviation of 7.4% in one case (Table II).

Table I. Comparison of Microbiological and Chemical Methods

(Pure material and tablets)

	Sample	Microbiological Assay, %	Chemical Assay, %	Deviation, %
1	Panthenol	99	97	−2.0
2	Panthenol	104	97	−7.0
3	Panthenol	99	103	+4.0
4	Panthenol	100	99	−1.0
5	D-Calcium pantothenate	96	98	+2.0
6	D-Calcium pantothenate	100	98	−2.0
7	D-Calcium pantothenate	100	98	−2.0
8	D-Calcium pantothenate	99	98	−1.0
9	D-Calcium pantothenate	100	100	0.0
		Mg./tablet		
10	Panthenol tablets	168	161	−4.2
11	Panthenol tablets	146	153	+4.8
			Av.	2.7

Table II. Comparison of Microbiological and Chemical Methods

(Panthenol ampoules)

Sample	Microbiological Assay, Mg./Ml.	Chemical Assay, Mg./Ml.	Deviation, %
1	101	103	+2.0
2	105	103	−1.9
3	101	102	+1.0
4	99	102	+3.0
5	104	104	0.0
6	26	25	−3.9
7	25	25	0.0
8	26	25	−3.9
9	26	25	−3.9
10	27	25	−7.4
		Av.	2.7

When assaying for panthenol, the microbiological method can be omitted if an ion exchange resin column is used, as described under "Assay of Panthenol in Multivitamin Preparations."

Experiments were conducted in order to determine the pH level at which no pantoic acid would occur. Samples of panthenol and calcium pantothenate at concentrations of 5 mg. per ml. were buffered with 0.1 molar acetate buffer at pH levels 4.2, 4.7, 5.2, 5.9, and 6.7 and sealed in ampoules. These ampoules were placed in an oven at 45° C. for a period of 6 weeks and assayed colorimetrically for panthenol and preformed pantoyl lactone and microbiologically for the presence of pantoic acid. At a pH of 6.7, 10% of the calcium pantothenate and 6.5% of panthenol had changed into pantoic acid. However, at pH levels 5.9 and below, no significant quantities of pantoic acid were found in any of the ampoules. These results indicate that microbiological assays are not necessary at a pH level below 5.9, for the only measurable hydrolysis product is pantoyl lactone. As is apparent in Figure 9, panthenol showed a loss of 17.5% in potency after 6 weeks at 45° at a pH of 4.2, while 89% of the calcium pantothenate had hydrolyzed to pantoyl lactone. These data are in good agreement with the findings of Rubin (*8*) obtained by means of curative bioassay in rats.

PRECISION OF METHOD

Samples of panthenol tablets and panthenol ampoules were assayed in duplicate on six different days by the method previously described. Good reproducibility was obtained with a maximum deviation of 2.8% from the mean (Table III).

ASSAY OF PANTHENOL IN MULTIVITAMIN PREPARATIONS

Experimental. When the method was applied to other vitamins, no color was obtained with thiamine hydrochloride, riboflavin, niacinamide, biotin, and folic acid either before or after hydrolysis. Pyridoxine hydrochloride produced a slight brownish color of the same intensity before and after hydrolysis. Ascorbic acid, however, produced considerable interference in this determination.

Because panthenol is a nonionic compound, it was thought that it could be separated from ascorbic acid and any other ionic substance by adsorption of these substances on an ion exchange column. One milliliter of a solution containing 65 mg. of ascorbic acid and the following vitamins of the B complex family—thiamine, riboflavin, pyridoxine, niacinamide—was applied to an Amberlite resin column IRA-400-OH and eluted with 100 ml. of water. The eluate was clear and colorless. When the previously described method was applied to this solution, no color was obtained, showing that all interfering substances had been absorbed on the column. In other experiments known quantities of pantoic acid, pantoyl lactone, and panthenol were added individually and combined to the previously described multivitamin solution and applied to the column. The eluate was assayed colorimetrically. The results are shown in Table IV.

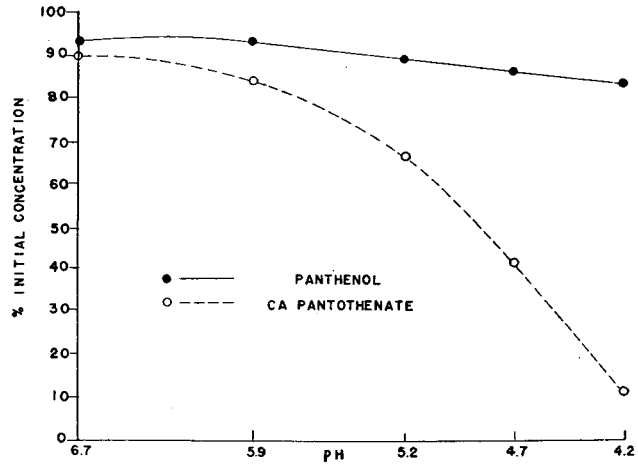

Figure 9. Stability of Panthenol Solutions and Calcium Pantothenate Solutions after 6 Weeks at 45° C.

It is evident that pantoic acid and pantoyl lactone are completely adsorbed on the resin column, while panthenol is quantitatively eluted. This modification renders the method specific for panthenol, because all ionic substances, which might produce a color, are removed from the sample solution. Calcium pantothenate also is adsorbed on the resin column and thus it is possible to differentiate between pantothenate and panthenol.

Table III. Reproducibility of Results

	Panthenol Tablets		Panthenol Ampoules	
Assay	Mg./tablet found	Deviation from mean, %	Mg./ml. found	Deviation from mean, %
1	162	+1.0	225	−0.7
2	161	+0.4	226	−0.3
3	159	−1.0	222	−2.1
4	163	+1.5	233	+2.8
5	161	+0.4	230	+1.5
6	162	+1.0	229	+1.0

Table IV. Panthenol in Multivitamin Preparations

Added, Mg.		% Recovered, Calculated as Panthenol
Pantoyl lactone	3	0
Pantoic acid	4	0
Panthenol	5.7	98
Panthenol	2.9	101.5
Pantoyl lactone	1.5	
Pantoic acid	2.0	99
Panthenol	2.9	

Procedure for Determination of Panthenol in Multivitamin Preparations. APPARATUS. The resin column is a glass tube of 14-mm. diameter and an over-all length of 200 mm., having a stopcock at the lower end. The column is fitted with a plug of fiber glass above the stopcock and is filled to a height of 40 mm. with Amberlite IRA-400-OH (obtainable from Rohm & Haas Company, Resinous Products Division, Philadelphia 5, Pa., or from Fisher Scientific Company).

CHARGING OF COLUMN. The column is treated with successive portions of 2 *N* hydrochloric acid (total about 50 ml.), washed with about 25 ml. of water, and then charged with about 50 ml. of 10% sodium hydroxide. The excess sodium hydroxide is thoroughly removed with successive water washings (total about 50 ml.). With about 10 ml. of water still present on top of the column, a thin glass rod is inserted and the resin is thoroughly stirred, so as to remove all bubbles. A small plug of fiber glass is then inserted on the top of the column. The excess water is drained off until a water layer of about 5-mm. height remains on top of the column, whereupon the stopcock is closed. This resin column may be recharged after use by the procedure described.

Instrument and reagents are as described above.

A standard solution of D-panthenol, 1.0 mg. per ml., is assayed against U.S.P. reference standard D-calcium pantothenate by the method described previously.

Procedure for Multivitamin Ampoule Solutions. An aliquot of the ampoule solution (1 to 3 ml.), equivalent to 2 to 3 mg. of panthenol, is pipetted onto each of three charged resin columns, marked, *A*, *B*, and *C*. To column *B* 1.0 ml. of standard solution containing 1 mg. of panthenol and to column *C* a standard containing 2 mg. of panthenol are added. It is advantageous to keep the total volume of solution, added to the column, as small as possible. The solutions are allowed to proceed through the columns at a rate of flow of 0.5 ml. per minute, until no liquid remains on top of the columns. Each column is then eluted with approximately 80 ml. of water, flowing at a rate of 3 ml. per minute. The eluates are collected in individual 250-ml. Erlenmeyer flasks and are evaporated to a volume of 10 ml. on a steam bath, using a stream of air to hasten the evaporation. To each flask 3 ml. of 1 *N* hydrochloric acid are added, the solution is hydrolyzed, and the panthenol is determined colorimetrically according to the technique described previously.

Preparation of Blank. Because any pantoyl lactone or pantoic acid that may be present is adsorbed on the column, a determination of either one is not necessary. In those cases where the eluate from the resin column is clear and colorless, only one blank is required.

It is prepared by titrating 2 ml. of hydroxylamine–sodium hydroxide reagent and 5 ml. 1 *N* sodium hydroxide followed by 3 drops of 2,4-dinitrophenol indicator with 1 *N* hydrochloric acid to a colorless end point and making up the volume to 50 ml. with water. A 5-ml. aliquot of this blank is pipetted into a colorimeter tube, followed by 1 ml. of 2% ferric chloride. The solution is mixed and the test tube is gently tapped on the table top just prior to the insertion of the tube into the colorimeter, which is set at 0 absorbance with this blank.

Calculation.

$$\frac{A \times D}{(B + C) - 2A \times E} = \text{mg. of panthenol per ml. of sample solution}$$

where

A = reading of sample solution
B = reading of sample plus 1 ml. of panthenol standard added
C = reading of sample plus 2 ml. of panthenol standard added
D = mg. of panthenol standard added to $B + C$
E = ml. of aliquot of sample solution used

Where the eluate from the resin column is slightly turbid or colored, the instrument is set at 0 absorbance with water and galvanometer readings of two blanks are taken.

Blank I (reagent blank) is prepared in the manner described previously.

Blank II (sample blank) consists of 5 ml. of the sample solution, the absorbance of which is read before addition of the ferric chloride reagent. In this case, the sum of the readings of blank I and blank II is subtracted from the reading of *A*, *B*, and *C*.

Procedure for Multivitamin Capsules with an Oil Base. A number of capsules, equivalent to about 40 mg. of panthenol, are carefully cut in half with a sharp razor blade and placed in a dry 250-ml. glass-stoppered Erlenmeyer flask. Any capsule mass remaining on the blade is removed with a small piece of filter paper which is added to the flask. Fifty milliliters of petroleum ether and exactly 25.00 ml. of water are added and the flask is agitated in a mechanical shaker for 1 hour. By means of a pipet most of the aqueous layer is transferred to a 50-ml. centrifuge cup and centrifuged for 5 minutes at about 3000 r.p.m. Ten to 15 ml. of the aqueous layer are carefully removed with a pipet and filtered through a Whatman No. 2 filter paper of 9-cm. diameter. The filtrate is collected in a test tube and exactly 2 ml. of the filtrate are pipetted onto each of three charged resin columns, marked *A*, *B*, and *C*. The determination is continued as described for ampoule solutions, beginning with "To column *B* 1.0 ml. of standard solution."

Multivitamin tablets and aqueous preparations, containing no appreciable quantities of oils, may be assayed by the method as described for ampoule solutions. However, if considerable quantities of oily constituents such as vitamin A are present, their removal with petroleum ether by the technique outlined for capsules is advantageous.

Table V. Panthenol Found in Multivitamin Preparations

Sample	Microbiological, Mg./Ml.	Chemical, Mg./Ml.	% Deviation
Solution, containing vitamin C and B complex vitamins			
1	3.3	3.2	−3.0
2	3.3	3.45	+4.5
3	3.1	3.2	+3.0
4	1.3	1.35	+4.0
	Mg./Capsule	Mg./Capsule	
Gelatin capsules, containing vitamins A, D, E, C, and B complex vitamins			
5	3.6	3.7	+2.8
6	3.6	3.5	−2.8
7	3.6	3.7	+2.8
8	14.5	13.9	−4.1
9	12.7	13.2	+3.9
10	9.9	9.7	−2.0
11	7.7	7.4	−3.9
Gelatin capsules, containing vitamin A, liver concentrate, and B complex vitamins			
12	5.8	5.9	+1.7
		Av. deviation	3.2

Results. The chemical method, described above, was applied to a number of different commercial multivitamin preparations and compared with results obtained by the microbiological method (Table V).

Good agreement between the two methods of assay was found, with an average deviation of 3.2%.

ACKNOWLEDGMENT

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Estimation of Streptomycin in Fermentation Broths

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An ion exchange procedure is presented for the chemical estimation of streptomycin in fermentation broths. The method is suitable for plant control purposes.

STREPTOMYCIN present in a fermentation broth cannot be assayed directly by the maltol assay method of Titus and Fried (*5*) because of the presence of interfering substances, but may be assayed biologically, or more rapidly by the sodium cotton succinate ion exchange method of McIntire and Schenck (*3*, *4*), or by the method of Boxer, Jelinek, and Leghorn (*1*), in which the maltol formed by degradation of the streptomycin is extracted with an organic solvent before colorimetric assay. [Attention has been drawn to an alternative maltol assay method which has been recently published by Eisenman and Bricker (*2*).] The authors have developed an assay method, suitable for plant control work, using the carboxylic-type cation exchange resin, Amberlite IRC-50 (a product of the Rohm & Haas Company, Philadelphia, Pa.) combined with the maltol assay procedure.

EXPERIMENTAL

Apparatus and Preparation. The apparatus used is shown in Figure 1.

Sufficient of the sodium form of the washed resin, prepared by equilibrating the hydrogen form of the resin with three of four successive lots of a saturated sodium bicarbonate solution, was introduced into an adsorption tube 4 mm. in diameter with sufficient saturated sodium bicarbonate solution to give a 1-cm. head of solution above a 12-mm. resin column. After the resin bed had been stirred thoroughly to remove air bubbles, a glass wool pad was placed above it and the funnel attachment was fitted. The streptomycin broth was diluted with a 0.2 *M* disodium hydrogen phosphate solution to a potency of 20 to 50 units per ml., adjusted to pH 8.5 to 9 with a 0.2 *N* sodium hydroxide solution, and clarified by centrifuging.

Adsorption. Distilled water (0.5 ml.) followed by the prepared broth (5 ml.) and wash water (1 ml.) were consecutively percolated through the resin bed at a flow rate not exceeding 0.3 ml. per minute. The streptomycin cations were quantitatively adsorbed by the resin at this pH.

Elution. Immediately after the wash water had drained from the funnel, 25 ml. of a 0.2 *N* hydrochloric acid solution were passed through the column at a flow rate of 0.5 ml. per minute. The first 20 ml. of effluent, which contained the eluted streptomycin free from interfering substances, were collected for chemical assay.

Chemical Assay. The streptomycin was hydrolyzed to form maltol by adding 0.2 ml. of a 4 *N* sodium hydroxide solution to 4-ml. aliquots of the acid eluate. These were heated in a boiling water bath for exactly 6 minutes, and then immediately cooled to room temperature in an ice bath. Evaporation losses were minimized according to the procedure of Titus and Fried. The ultraviolet absorption at 322 mμ of each aliquot before and after heating was measured in a 1-cm. cell in a Beckman spectrophotometer. The difference between the two readings, ΔD, was converted to the potency of the original streptomycin solution by referring to curve 4 in Figure 2.

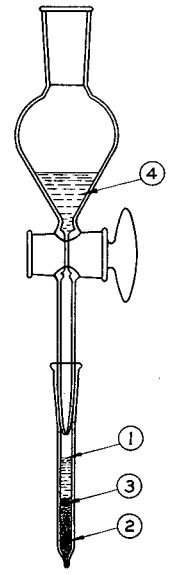

Figure 1. Resin Adsorption Column and Attached Reservoir

1. Liquid head
2. Resin bed
3. Glass wool pad
4. Reservoir

DISCUSSION

The slope of the linear relationship between ΔD and the potency of the streptomycin solution under examination depends on the strength of the alkali used for hydrolysis, and on the order of purity of the streptomycin in the original sample. This relationship was determined using Food & Drug Administration (F.D.A.) standard streptomycin containing 400 units per mg. and 2 *N*, 4 *N*, and 6 *N* sodium hydroxide solutions for the hydrolysis. The results are plotted in curves 1, 2, and 3 in Figure 2. Samples of broth at various concentrations were assayed by the above method using a 4 *N* sodium hydroxide solution for the hydrolysis. The eluates obtained were diluted to various concentrations and their ΔD values compared with the broth potency obtained by biological assay. Application of the method of least squares to the results from thirty samples examined yielded the following relationship between ΔD and the broth potency, *P*:

$$\Delta D = 0.0147\ P + 0.0178$$

which is shown as curve 4, Figure 2. This calibration curve gave more reproducible results than the corresponding curve

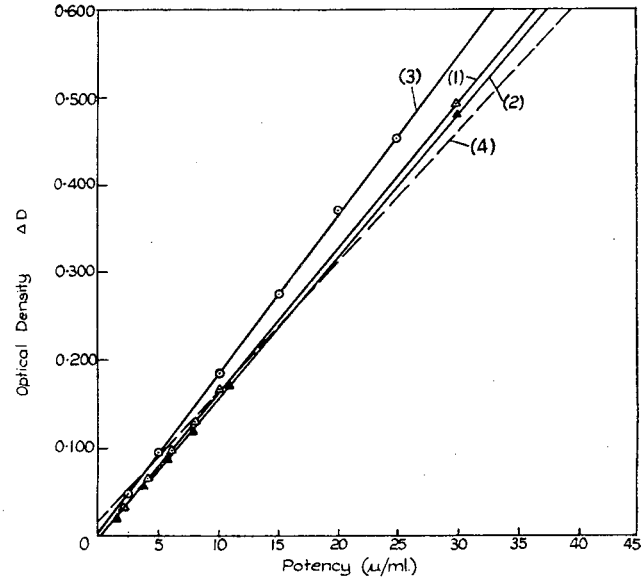

Figure 2. Variation of Optical Density with Potency of Streptomycin Sulfate Solutions

Various strengths of sodium hydroxide used for maltol reaction with aqueous solutions of F.D.A. streptomycin

1. 2 *N* NaOH
2. 4 *N* NaOH
3. 6 *N* NaOH
4. Best-fit line for broth eluate samples

obtained for the purer F.D.A. standard streptomycin (curve 2, Figure 2). If the method is to be applied to a variety of types of streptomycin broth individual calibration curves must be constructed for each system.

To determine the relative proportion of streptomycins A and B in a mixture, Schenck *et al.* (*4*) have utilized the fact that streptomycin B gives more maltol per unit of biological activity than streptomycin A. Because the above results show close

agreement between the chemical and biological methods, the broths used in the present work did not contain appreciable amounts of streptomycin B.

When the resin was prepared by equilibrating with phosphate buffer solution at pH 7 in place of the saturated sodium bicarbonate solution, the eluates from the streptomycin broth showed apparent recoveries of 130 to 170%. The recovery of streptomycin from the adsorption column was determined from a comparison of the potency of the original broth, determined biologically, with that derived from the maltol reaction of the eluate. Inasmuch as the ultraviolet absorption of each aliquot was measured at 322 mμ before and after heating, the high recoveries obtained indicate the presence of biologically inactive substances in the broth which hydrolyze to give an absorption at 322 mμ, and, as the results obtained with the sodium bicarbonate equilibrated resin at pH 9 showed recoveries of 100%, these substances have a lower basic strength than streptomycin A.

The assay method described, employing adsorption at pH 9 and hydrolysis with 4 *N* sodium hydroxide, yields results which agree with the biological assay method to within ±5%. The reproducibility of a single chemical assay is ±3%.

ACKNOWLEDGMENT

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Identification of Coupling Components in *p*-Toluene-Azoaryl Amide Dyes of Naphthol AS Series

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A simple method has been developed for the identification of aminonaphthol AS type reduction products, by hydrogenating the pigment in dioxaneacetic acid with zinc dust, isolating the desired compound, and converting it to the *N*-benzoyl derivative.

THE amides resulting from the condensation of 2-hydroxy-3-naphthoic acid with aromatic primary amines constitute a very important group of coupling components known as the Naphthol AS intermediates. When treated with a diazonium salt, they give rise to a class of dyes which finds wide application in the textile and printing ink industries.

Unknown colors falling in this category are usually analyzed by reductive fission of the azo bond, followed by isolation and identification of the resulting products. This reaction normally splits the monoazo pigment into two fractions, the original amine and the amino derivative of the aryl amide, or their respective diamines or possibly triamines, if nitrated.

Procedures for the characterization of the former compounds are fairly numerous (*2–4*, *6–9*), but except for the work of Battegay, Langjahr, and Rettig (*1*) on the synthesis of 1-aminonaphthol AS from 1-nitrosonaphthol AS and from phenylazonaphthol AS, and by Koch and Milligan (*4*) on the identification of unsulfonated dyes made with Naphthol AS, the chemical journals are practically devoid of analytical data regarding the latter products.

This paper, in an effort to bridge this gap, describes the hydrogenation of these colors with zinc dust, in dioxaneacetic acid, followed by isolation of the aminoaryl amides, which are subsequently converted into their *N*-benzoyl derivatives. Confirmation of the aminonaphthol AS group of scission products will be found in another report (*5*) which is based on the work of Battegay and co-workers (*1*). By a modification of their method, the 1-nitroso compounds of the known commercial Naphthol AS intermediates were successfully synthesized, and these gave, on reduction, amines identical with those obtained in this paper.

GENERAL PROCEDURE

Preparation of Dyes. Diazotized *p*-toluidine was coupled to twelve Naphthol AS intermediates, obtained from E. I. du Pont de Nemours & Company, and the resulting pigments were dried without further purification.

Preparation of Reduction Products. A finely ground 2-gram sample of coloring matter and 10 grams of zinc dust are placed in a 250-ml. Erlenmeyer flask, and the solids are suspended in a solution of 50 ml. of dioxane plus 10 ml. of glacial acetic acid. Heat is applied, and the mixture is refluxed gently until the dye particles are decolorized. The hot reaction mixture is filtered to remove insoluble matter, which is then washed with 25 ml. of dioxane, and the filtrate is acidified with 50 ml. of hydrochloric acid to precipitate the aminonaphthol AS hydrochloride.

Maximum yield of the addition product is achieved by cooling overnight, and the solid is then collected on a Büchner funnel, washed with a small volume of dioxane, and transferred to a 500-ml. extraction funnel with approximately 50 ml. of ethyl alcohol. Buffering the suspended hydrochloride with 10 ml. of a 10% sodium acetate solution liberates the free amine, which may wholly or partially dissolve in the alcohol. The mixture is diluted with 250 ml. of ether, and any precipitate that may remain is solubilized by further buffering with 200 ml. of a 2.5% sodium acetate solution. Several water washings are applied to the ether layer, which is then dried with anhydrous sodium sulfate, filtered, and evaporated to near dryness.

Resolution of the ether residue is effected with 50 ml. of hot benzene, and incipient crystallization or cloud formation of the aminoaryl amide is attained by dilution with petroleum ether. Cooling the solvent mixture overnight precipitates the desired compound as yellow to greenish crystals, which are collected and purified by dissolving in benzene and precipitating again in the afore-mentioned manner.

Occasionally, the aminonaphthol AS product cannot be dissolved in ether. When this occurs, 100 ml. of benzene and 50 ml. of xylene are added to the ether layer, after the water wash, and

Table I. Identification of Naphthol AS Type Coupling Components[a]

	Condensation Product of 2-Hydroxy-3-naphthoic Acid with	Commercial Name	Melting Point of 1-Amino Reduction Product (Uncor.), ° C.	Nitrogen Content Calcd., %	Nitrogen Content Found, %	Melting Point of Benzoyl Derivative of Reduction Product (Uncor.), ° C.	Nitrogen Content Calcd., %	Nitrogen Content Found, %
1	Aniline	Naphthol AS	190–2[b]	...	...	268–70	7.33	7.35
2	*o*-Toluidine	Naphthol ASD	162–4	9.58	9.38	232–3	6.98	6.79
3	*m*-Xylidine	Naphthol ASMX	166–8	9.15	9.08	241–2	6.83	6.88
4	*o*-Anisidine	Naphthol ASOL	161–3	9.09	8.96	228–30	6.79	6.65
5	*p*-Anisidine	Naphthol ASRL	160–2	9.09	8.93	249–50	6.79	6.56
6	*o*-Phenetedine	Naphthol ASOP	151–3	8.70	8.44	211–13	6.57	6.72
7	1-Naphthylamine	Naphthol ASBO	201–3	8.54	8.40	258–9	6.48	6.37
8	2-Naphthylamine	Naphthol ASSW	184–6	8.54	8.51	269–70	6.48	6.44
9	*m*-Nitroaniline	Naphthol ASBS	183–5[c]	14.33	14.24	310–11[d,e]	8.38	8.27
10	*p*-Chloroaniline	Naphthol ASE	160–2[f]	8.96	9.00	279–81	8.52[g]	8.55[g]
11	5-Chloro-*o*-toluidine	Naphthol ASTR	182–4	8.58	8.51	263–4	8.25[g]	8.28[g]
12	5-Chloro-2,4-dimethoxy aniline	Naphthol ASITR	215–17	7.52	7.36	245–6	5.88	5.84

[a] Mixed melting points with known products will differentiate between compounds such as 1-aminonaphthol ASD and 1-aminonaphthol ASOL.
[b] M.p. literature, 188–90° C.
[c] Diamine formed by reduction of nitro group on condensing amine.
[d] Dibenzoyl derivative.
[e] Extremely insoluble in solvents such as dioxane, glacial acetic acid, and xylene. Purified by leaching with boiling acetic acid.
[f] Showed tendency to darken and eventually decompose during repeated recrystallization.
[g] Chlorine content.

the combined solvents and insoluble matter are evaporated until only xylene remains. The aminoaryl amide, which will now be in solution, is precipitated with petroleum ether as previously described.

Preparation of *N*-Benzoyl Derivatives. The aminonaphthol AS products are refluxed with 1.5 grams of benzoic anhydride in 30 to 50 ml. of xylene for 2 hours, and cooled overnight. The *N*-benzoyl derivative separating out is filtered off, washed with alcohol, and crystallized from glacial acetic acid.

All melting points were taken with a standard 360° C. thermometer immersed in a Thiele tube filled with dioctyl phthalate. Customary precautions regarding heating rate and thermometer immersion depth were carefully followed.

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Photoelectric Determination of Atmospheric Sulfur Dioxide

Employing Dilute Starch-Iodine Solutions

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THE early methods for determining the concentration of sulfur dioxide in air were more suitable for flue gas analysis than for the low concentrations ordinarily found in urban and smelter areas.

The first method adapted to the rapid determination of small amounts of sulfur dioxide in air was that used by Marston and Wells in the investigation carried out by the Selby Smelter Commission (*5*). Measured volumes of air were drawn into a partly evacuated 24-liter aspirator bottle. A definite amount of starch solution containing sufficient iodine to bring the reagent to a desired blue color was added, and the aspirator bottle was shaken vigorously to bring the air sample in contact with the starch-iodine solution. The color of the partly bleached iodine solution was then restored by the addition of standard iodine reagent so as to match that of a blank similarly treated. Reasonably close checks were obtained against known mixtures of sulfur dioxide in air in the range of 0.80 to 3.00 p.p.m. With lower or higher concentrations the errors were as high as 20 to 25%. This method, with certain modifications, was used by Monnett (*10*) in his survey of atmospheric conditions at Salt Lake City, in the investigation by the Swain Commission (*12*), and later by McKay and Ackermann (*8*).

The preparation of stable iodine solutions is important in methods of this type, because a rapid stream of pure air passed through an aqueous iodine solution will soon weaken the strength of the solution. If, on the other hand, the vapor pressure of the iodine in solution is repressed by the addition of potassium iodide and starch, solutions may be made that are remarkably stable even after prolonged aspiration with air. Zepf and Vetter (*19*) investigated the stability of very dilute iodine solutions and showed that a certain minimum quantity of both starch and potassium iodide was necessary to eliminate loss from a 0.0001 *N* iodine solution.

A distinct advance over the method of Marston and Wells was made by Thomas (*13–17*), who developed not only a portable apparatus for the rapid measurement of small concentrations of sulfur dioxide in air but also a continuous automatic method which has become widely used in recent years. Thomas and Cross (*15*) investigated the stability and efficiency of iodine solutions for absorbing sulfur dioxide. When 28 liters of pure air were aspirated through 100 ml. of 0.0011 *N* iodine solution, containing 2 grams of potassium iodide and 1 gram of starch per liter, the loss of iodine was about 4%. Only about half of this material was caught in the second absorber. A 0.0006 *N* solution was changed only about 1% by this treatment and more dilute solutions were very stable. A 0.000075 *N* solution did not change when 400 liters of air were drawn through it.

The iodine method advocated by Thomas involved the use of an absorbing solution of 0.0005 *N* iodine, containing 1 gram of

Dilute solutions of starch-iodine have been found suitable for the continuous determination of low concentrations of sulfur dioxide in smelter areas where hydrogen sulfide is not likely to occur. The most effective concentration range of solution is from about 7×10^{-5} N to 2×10^{-5} N. The apparatus for the continuous recording of sulfur dioxide consists of a Thomas analyzer, two gas bubblers containing 100 ml. of solution mounted in a block with a light source between them, and two photoelectric cells. The output current is passed through a standard resistance box and the voltage drop across the 0 to 500-ohm terminals is measured by a potentiometer with a scale range of 0 to 50 mv. The instrument has a range of less than 0.01 to 1.00 p.p.m. or more, depending upon the size of the gas sample and the volume of solution used in the absorbers. It has been used for several seasons to determine the sulfur dioxide content of the air at a location in the Sudbury smelting district. Comparative tests of the iodine and hydrogen peroxide conductivity methods have been made with a portable apparatus on simultaneous samples of air in the path of the smelter fumes. The results indicate that a substantial fraction of the smelter smoke during a fumigation may consist of sulfur trioxide, sulfuric acid, or sulfate.

starch and 2 grams of potassium iodide per liter. After aspiration with the required amount of air at the rate of about 10 liters per minute, the iodine solution was titrated with 0.002 N sodium thiosulfate solution. In his first paper on this subject, Thomas described a semiautomatic apparatus for the determination of low concentrations of sulfur dioxide in air; iodine solutions of the above type were used. The method is applicable over the range of concentrations from 0.10 to 60 p.p.m.

Ellis (*3*) has described two methods for the determination of sulfur dioxide in air. The first method, which was used for measuring the titratable acidity of the air, utilized a solution of Hyperol, the solid compound of hydrogen peroxide with urea, in water. In the second method, similar to that advocated by Thomas and Cross, iodine, potassium iodide, and starch solution were employed as the absorbant. Ellis found that 0.0005 N iodine solution containing 2 grams of potassium iodide per liter was remarkably stable. He suggested that the dissipation, even in the dark, of the approximately 0.0003 N iodine solutions used by Marston and Wells was due to insufficient potassium iodide. Furthermore, he found that 0.002 N thiosulfate solution, when carefully made up, maintained its concentration unchanged for 37 days, whereas that of an arsenite solution dropped progressively during this period. All solutions were kept dark when not in use.

A method described by Smith and Friis (*11*) consisted in absorbing the sulfur dioxide in 50 ml. of 0.1 N sodium hydroxide. The sodium hydroxide solution was then neutralized with 6 ml. of 1 N hydrochloric acid, 1 ml. of starch solution was added, and the mixture was titrated with 0.001 N iodine solution to a blue end point. A comparison was made with a blank determination, carried out to a similar end point. This method was used by the Mellon Institute in surveys of the air in various industrial centers (*9*).

The method used by the author (*7*) in measuring sulfur dioxide concentrations with a portable apparatus in the Trail area, and also in the Windsor-Detroit area, was based on that of Thomas and Cross with the modification by Griffin and Skinner (*4*) involving the use of a soda-lime tower in connection with the blank determinations.

The apparatus consisted of an accurately calibrated flowmeter connected to two absorbers of 350-ml. capacity. The flowmeter and absorbers with the appropriate stopcock connections, two 100-ml. automatic pipets for delivering an exact volume of absorbent, a microburet of 10-ml. capacity, for titrating the aspirated solutions, a thermometer, and portable barometer were mounted in a wooden box. Suction was obtained by attaching this apparatus to the exhaust manifold of the automobile in which the equipment was transported; a small surge tank, equipped with needle valves, was placed between the portable apparatus and the connection to the exhaust manifold. A small battery-operated pump may also be used as a source of suction. The flowmeter consisted of a small length of capillary tubing connected to a U-tube and calibrated according to the method of Benton (*1*). The absorbent, a stabilized 5×10^{-5} N starch-iodine solution, was aspirated with air at a rate of about 10 liters per minute. The time taken for a single determination was usually about 6 to 8 minutes. The aspirated solutions were titrated with 0.001 N sodium thiosulfate to a light blue color. Blank determinations were made on sulfur dioxide–free air, the solution being titrated to a similar end point.

Thomas and his associates have developed analyzers for the continuous, automatic determination of low concentrations of sulfur dioxide in air (*13*, *14*, *16*, *17*) based on the change in conductivity of acid–hydrogen peroxide solutions. The solution contains 0.003% hydrogen peroxide and 0.0005% sulfuric acid. The amount of sulfur dioxide absorbed is indicated by the increased conductance of the solution as recorded by a Leeds & Northrup Wheatstone bridge of the Micromax type. The system is calibrated with solutions of sulfuric acid of known normality.

The method is not specific for sulfur dioxide and may also indicate the presence of sulfuric acid or sulfate. The introduction of a heated platinum wire catalyst in the air-inlet line has extended this method to the determination of other sulfur contaminants such as hydrogen sulfide, mercaptans (thiols), and other volatile organic sulfur compounds which may be present in small amounts of city air.

The present paper describes a continuous, automatic analyzer for sulfur dioxide which employs photoelectric cells and a recording potentiometer to indicate the increase in light transmittance of stable, blue, starch-iodine solutions after aspiration with contaminated air. The method is specific for sulfur dioxide in smelter areas where hydrogen sulfide is not likely to occur.

The instrument has a range of less than 0.01 to 1.00 p.p.m. or more, depending upon the volume and concentration of the solution in the absorbers and the amount of air sample passed through the solution.

CONTINUOUS PHOTOELECTRIC SULFUR DIOXIDE ANALYZER

The main features of the continuous photoelectric analyzer which was operated for several growing seasons in the Sudbury nickel smelting district at a point about 60 miles northeast of Copper Cliff, Ontario, were as follows:

A Thomas analyzer (*13*) was employed to measure and discharge a definite volume of absorbant solution into two gas bubblers consisting of borosilicate glass salvarsan tubes of 350-ml. capacity. This instrument operated on a 2-minute time cycle, the solution in one absorber being aspirated at a measured flow rate for this interval, after which the air was passed through the second absorber, by the opening and closing of appropriate cam-operated poppet valves. The aspiration was continued alternately for eight successive operations in each absorber. At the end of this period of about 32 minutes the solution in each absorber was drained successively and fresh solution was delivered from a stock bottle of about 20-liter capacity. The light transmittance through the blue starch-iodine solution was recorded during the 2-minute quiescent period following each aspiration

cycle by means of a Leeds & Northrup recording potentiometer with a scale range of 0 to 50 mv.

Preliminary experiments indicated that the following dilute starch-iodine solution remained stable after aspiration with sulfur dioxide–free air at rates of about 10 liters per minute for periods of 30 minutes or more.

One gram of soluble starch was dissolved in about 500 ml. of boiling distilled water in the usual manner. This was allowed to cool and transferred to a 1000-ml. volumetric flask. To it were added 2 ml. of 0.01 N sulfuric acid, followed by a solution containing 8.0 ml. of 0.01 N iodine and 2 grams of potassium iodide. The mixture was then made up to volume. If 100 ml. of this solution are completely decolorized by the sulfur dioxide contained in 22.4 liters of air at normal temperature and pressure, the concentration is equivalent to 4.0 p.p.m. by volume.

The change in concentration of the blue starch-iodine solution was determined by using two Weston photronic cells (Model 594) to measure the light transmittance through each absorber from a constant source, a 20-watt lamp connected to the 110-volt alternating current line through a constant-voltage transformer. The arrangement of this unit is shown in Figure 1.

The absorbers, light source, and photoelectric cells were mounted in a wooden block as shown, the exposed surfaces of the block along the light path being painted black. The light source was fixed midway between the two absorbers and a photocell was mounted behind each absorber. The output current from the cells was passed through a standard resistance box and the voltage drop across the 0 to 500-ohm terminals was measured by means of the recording potentiometer.

With the above 8×10^{-5} N iodine solution, illumination by the lamp gave a transmittance value or photocell output equivalent to about three scale divisions on the potentiometer chart, whereas with an almost completely decolorized iodine solution the chart reading was about 96—i.e., near the end of the scale.

The recorder was calibrated by determining the potentiometer readings for a series of starch-iodine solutions varying in normality from 8×10^{-5} to 2×10^{-5} during the operation of the analyzer on sulfur dioxide–free air. A typical calibration curve is shown in Figure 2.

The type of record obtained during the actual operation of the recording analyzer over a 32-minute cycle was similar to that of the Thomas conductivity analyzer operating on the same cycle. However, during the short interval of less than 2 minutes intervening between the cell draining and filling operation, the light beam passed through an empty absorber. This caused the potentiometer to record a full-scale deflection to nearly the end of the chart. This track provided a reliable guide to the regularity of mechanical operation of the analyzer. The method was extremely sensitive, concentrations of less than 0.01 p.p.m. being readily detected.

The type of record obtained during the progress of a fumigation in the field is shown in Figure 3. The concentrations may be calculated as average values over the whole cycle of 32 minutes or reported over 2-minute intervals. A smooth curve drawn through the 2-minute steps of the chart would indicate instantaneous values or other variations in intensity during a given fumigation in the field.

It was found preferable to make up the stock solutions to a concentration of 6×10^{-5} N with respect to iodine in order to secure greater sensitivity in the low sulfur dioxide concentration range. The location of the recorder station was sufficiently distant from the source of pollution so that concentrations in excess of 0.25 p.p.m. were present only at infrequent intervals; the highest recorded concentration was 0.52 p.p.m.

It was necessary to select the starch required for the stock solution with care. Only a high grade starch which gave the characteristic blue color with dilute iodine solution was suitable for this work. Grades that yielded a purple tinge were unsatisfactory. The stock solutions could be stored in a cool, dark room for upward of a week without appreciable deterioration, provided the vessels were maintained in a clean, sterile condition.

The method may be employed over a considerable range of sulfur dioxide concentration in field work. For a location where high concentrations of the order of several parts per million occur frequently, the range of the instrument may be extended by reducing the volume of gas sample or increasing the concentration of reagent. The low concentration range from 25 to less than 1 part per 100,000,000 can be adequately covered with a high degree of sensitivity by starch-iodine solutions having an initial concentration of 5×10^{-5} N.

In continuous operation the instrument should be recalibrated about once a month in order to check the response of the photoelectric cells. Any excessive fatigue in the cells can be readily

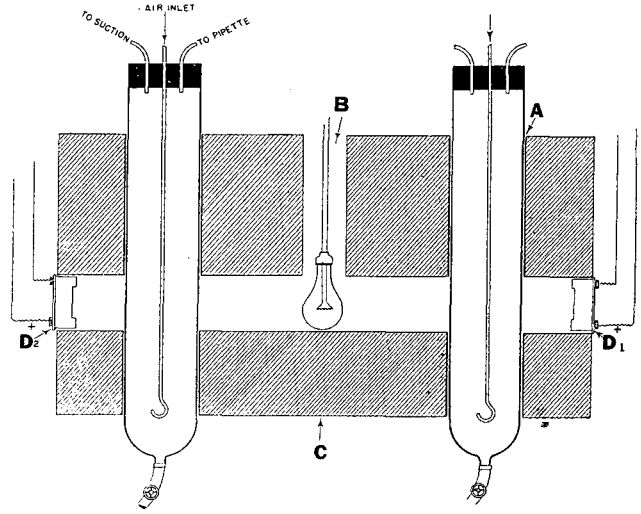

Figure 1. Diagram of Continuous Colorimeter Unit

A. Absorption tube containing dilute starch-iodine solution. *B.* Light source maintained at constant voltage. *C.* Wood mounting block. D_1/D_2. Weston photronic cells

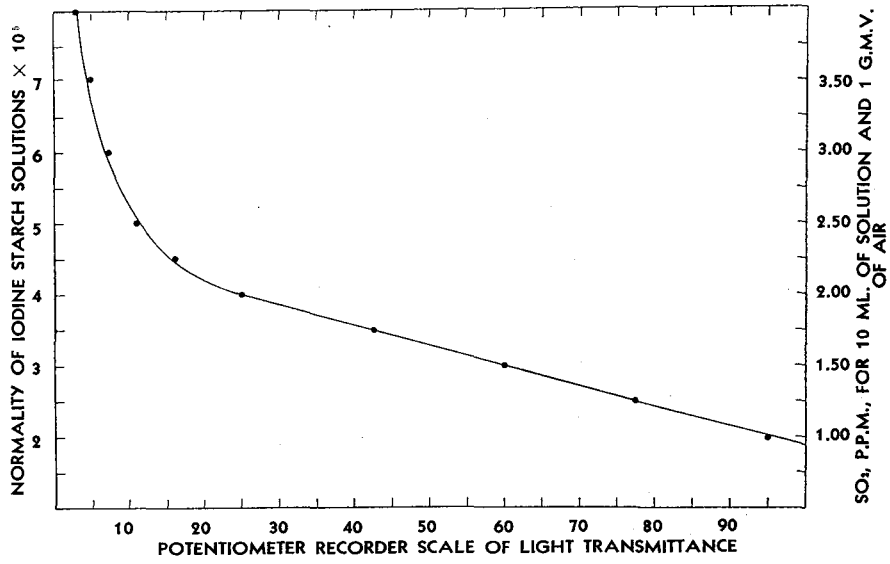

Figure 2. Calibration Curve Showing Relation between Potentiometer Scale of Light Transmittance and Normality of Starch-Iodine Solutions

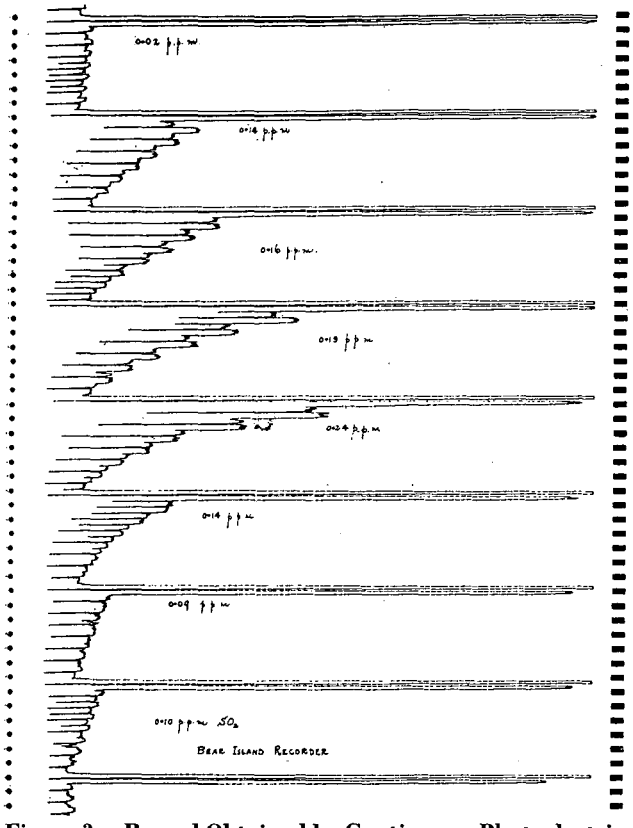

Figure 3. Record Obtained by Continuous Photoelectric Recorder during Sulfur Dioxide Fumigation in the Field

Reading from top to bottom, 0.02, 0.14, 0.16, 0.13, 0.24, 0.14, 0.09, and 0.10 p.p.m. SO_2

detected by the potentiometric readings corresponding to solutions of known normality. If calibrated at regular intervals, a pair of photoelectric cells will serve throughout a whole growing season on continuous operation.

The instruments are housed in a well insulated shelter of wood construction approximately 8 feet square by 7.5 feet high (inside dimensions) in order to avoid excessive temperature changes. In cool weather the shelter is heated by an electrical heater with thermostat control.

Observations by this photoelectric recorder on sulfur dioxide–free air indicated substantially constant zero readings during each cycle of operations. Reproducible results were obtained on iodine solutions of equivalent normality. The method is much more sensitive than the usual volumetric methods for the estimation of sulfur dioxide in low concentrations.

The method is specific for sulfur dioxide in smelter areas where hydrogen sulfide is not likely to be present in the atmosphere. It possesses certain advantages over the conductivity method employing dilute sulfuric acid solutions containing an excess of hydrogen peroxide. The latter method determines not only the sulfur dioxide but also sulfuric acid and sulfate, including that derived from sulfur trioxide. Because sulfur dioxide is much more toxic to plant life than equivalent concentrations of sulfuric acid mist or sulfate, an accurate knowledge of the sulfur dioxide content of the air by a specific method is sometimes necessary.

SIMULTANEOUS DETERMINATION OF SULFUR DIOXIDE, SULFUR TRIOXIDE, AND SULFATE

The accurate estimation of sulfur dioxide, sulfur trioxide, and sulfuric acid or sulfate in the smoke stream of a smelter area depends upon the simultaneous sampling of these products in a given atmosphere. Considerable information on the sulfur components of smelter smoke during gas visitations in the field may be obtained by the application of the starch-iodine and conductivity methods of analysis in portable sampling equipment. Such equipment has been used in the Sudbury nickel smelting area to determine concentrations at ground level and at various altitudes during flights in aircraft.

A simple diagram of the sampling unit is shown in Figure 4.

The essential features are two borosilicate glass absorbers fitted with carefully matched fritted-glass disks of medium porosity and a pair of accurately calibrated flowmeters of the capillary orifice type. The unit is of all-glass construction. Rubber connections are employed only to connect the suction line to the source of suction. The filling, aspiration, and drainage operations are performed by turning appropriate glass stopcocks. The flowmeters are constructed of the required dimensions of capillary tubing to operate in the region of turbulent flow. The volume of flow then varies inversely as the square root of the density of the gas. Calibration of the flowmeter is effected by connecting the apparatus to a precision wet-test meter, passing air in measured volumes through the system at the observed temperature and pressure, and noting the pressure differences of the liquid manometer attached to the capillary.

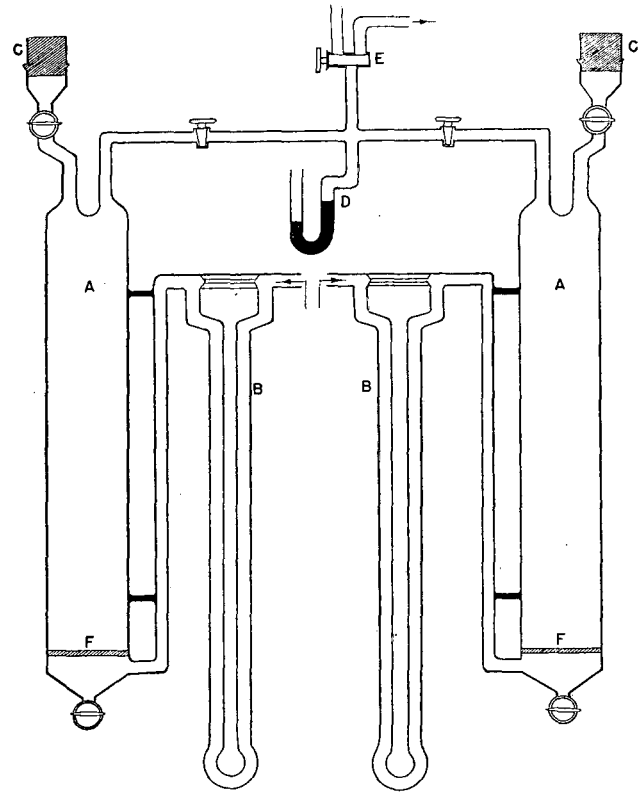

Figure 4. Sampling Unit for Simultaneous Determination of Sulfur Dioxide and Sulfuric Acid in Air

A. **Borosilicate glass absorbers**
B. **Matched pair of calibrated capillary flowmeters**
C. **Cups for delivering measured volume of reagent**
D. **Mercury U-tube to indicate vacuum on suction line**
E. **Three-way stopcock to connect with suction line or atmosphere**
F. **Fritted-glass disks of medium porosity sealed into absorbers**

Considerable changes in temperature and pressure are required to effect a major change in the rate of flow of this type of meter. Thus, at about 20° C. a decrease in pressure of 15 mm. of mercury, or an increase in temperature of about 6° C., is required to change the volume of flow by about 1%.

The equipment was mounted on a wooden panel, enclosed in a box, and transported by automobile or aircraft. The suction was provided by a connection to the windshield wiper or intake manifold line of the car, and the suction was regulated by a small metal surge tank equipped with needle valves. In field tests the automobile or truck was parked about 35 to 50 feet downwind and to one side of the test apparatus, so as to avoid contamination from exhaust fumes, and a long line of rubber tubing connected the suction manifold to the surge tank behind the sampling unit.

The air sample was divided equally between the two bubblers of the sampling unit, at the rate of 5.0 liters per minute through each absorber. This could be done easily by comparison of the manometer levels of the capillary flowmeters and by making a slight adjustment, if necessary, to balance the flow by means of one of the stopcocks. One absorber contained 25 ml. of 8×10^{-5} N starch-iodine solution made up as indicated for the

photoelectric recorder. The other absorber contained 25 ml. of dilute sulfuric acid–hydrogen peroxide solution (6×10^{-5} N containing 0.5 ml. of 30% hydrogen peroxide per liter). The solutions, after aspiration with measured volumes of air, were drained back into the corresponding glass-stoppered sample bottles and returned to the Sudbury laboratory for analysis. Observations were made of the flow rate, time of flow with a stopwatch, temperature, barometric pressure, and suction pressure. The total sampling time in each simultaneous test was 5 minutes.

When high concentrations were encountered, as indicated by the approaching decolorization of the starch-iodine solution, the sampling period was shortened. Blank determinations were made frequently by inserting a soda-lime tower in the inlet lines to the absorbers.

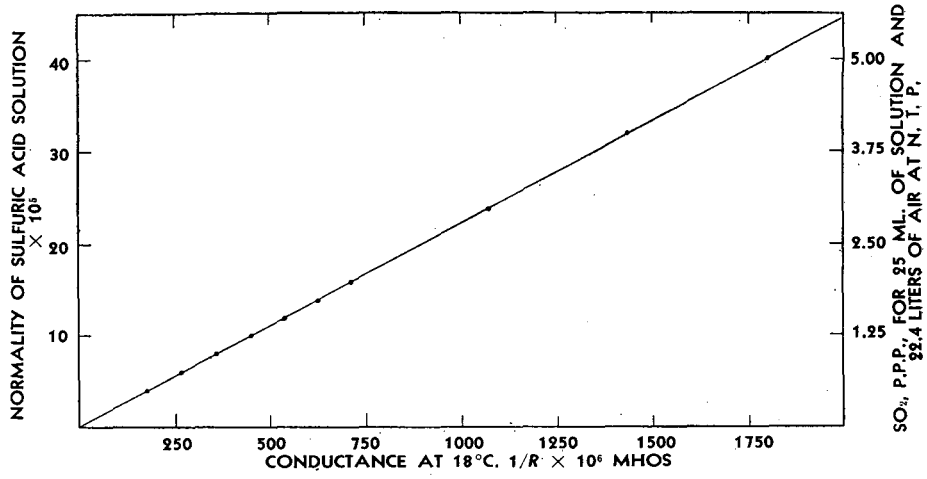

Figure 5. Relation between Conductance of Dilute Sulfuric Acid Solutions and Sulfur Dioxide Content of Air for Field Sampling Unit

The conductivity of the dilute sulfuric acid–hydrogen peroxide solutions was determined by a Wheatstone bridge, Model RC-8, Industrial Instruments, Inc. A typical calibration curve is shown in Figure 5. The iodine solutions were titrated with a microburet to a faint blue end point with freshly prepared and accurately standardized 0.001 N sodium thiosulfate, an aliquot of 20.0 ml. being taken from each bottle for this analysis. In an alternative method the increase in light transmittance of the blue solutions was determined in a calibrated colorimeter consisting of a Weston photronic cell, 6-volt 30-c.p. lamp, and a sensitive Jewell microammeter. The change in conductivity of the peroxide solutions and the decrease in strength of the iodine solutions in comparison with the blank determinations were calculated as parts per million of sulfur dioxide.

SULFUR COMPONENTS OF SMELTER SMOKE

The results of a large number of simultaneous observations by the starch-iodine and conductivity methods during field fumigations in the Sudbury area were grouped according to the character of the fumigations into heavy, medium, and mild smoke visitations. The number of observations in each smoke visitation, the average concentration by each method, and the difference representing sulfur trioxide, sulfuric acid, or sulfate are given in Tables I, II, and III. In all types of fumigations the conductivity values were consistently higher than the corresponding iodine values. Although the major fraction of the sulfur components of the smoke consisted of sulfur dioxide, appreciable, though variable, quantities of sulfuric acid or sulfate were present.

The results of fifteen heavy smoke visitations with an average of 1.096 p.p.m. of total sulfur contaminants (calculated as sulfur dioxide) indicated that the sulfur dioxide component represented 86.6% of the total. In twenty-two medium fumigations averaging 0.464 p.p.m., the sulfur dioxide content was 82.6%, and in thirteen fumigations of a mild character, at an average concentration of 0.2045 p.p.m., it represented 83.7% of the total.

The differences between the means were subjected to the t test and were found to be significant to better than the 0.01% level of probability.

Table I. Heavy Smoke Fumigations in a Smelter Area

(Simultaneous determinations of sulfur contaminants by starch-iodine and conductivity methods)

No. of Observations	Sulfur Contaminants by Conductivity Method Calcd. as SO_2, Av. Concn., P.p.m.	Sulfur Dioxide by Iodine Method, Av. Concn., P.p.m.	Average Difference, P.p.m.
5	0.948	0.902	0.046
8	0.900	0.622	0.278
12	0.776	0.686	0.090
10	1.600	1.195	0.405
4	1.680	1.649	0.031
11	1.665	1.540	0.125
5	0.781	0.706	0.075
17	1.010	0.940	0.070
5	1.317	1.069	0.248
8	0.855	0.716	0.139
6	1.044	1.010	0.034
8	1.158	0.970	0.188
5	1.152	1.013	0.139
13	1.320	1.085	0.235
23	0.793	0.705	0.088
Total 140	Av. 1.096	0.950	0.146

Table II. Medium Smoke Fumigations in a Smelter Area

No. of Observations	Sulfur Contaminants by Conductivity Method Calcd. as SO_2, Av. Concn., P.p.m.	Sulfur Dioxide by Iodine Method, Av. Concn., P.p.m.	Average Difference P.p.m.
9	0.495	0.457	0.038
9	0.403	0.262	0.141
8	0.515	0.411	0.104
30	0.366	0.275	0.091
8	0.324	0.290	0.034
10	0.584	0.503	0.081
17	0.518	0.414	0.104
23	0.395	0.376	0.019
6	0.303	0.262	0.041
5	0.490	0.398	0.092
10	0.422	0.316	0.106
7	0.703	0.528	0.175
7	0.547	0.487	0.060
16	0.380	0.303	0.077
13	0.368	0.348	0.020
11	0.356	0.263	0.093
16	0.580	0.452	0.128
9	0.626	0.520	0.106
15	0.680	0.665	0.015
5	0.491	0.308	0.183
10	0.532	0.410	0.122
6	0.430	0.334	0.096
Total 250	Av. 0.464	0.383	0.081

Table III. Mild Smoke Fumigations in a Smelter Area

No. of Observations	Sulfur Contaminants by Conductivity Method Calcd. as SO_2, Av. Concn., P.p.m.	Sulfur Dioxide by Iodine Method, Av. Concn., P.p.m.	Average Difference, P.p.m.
21	0.181	0.155	0.026
9	0.202	0.153	0.049
14	0.248	0.202	0.046
7	0.203	0.167	0.036
8	0.102	0.095	0.007
9	0.254	0.234	0.020
5	0.099	0.077	0.022
14	0.235	0.192	0.043
10	0.284	0.243	0.041
7	0.204	0.146	0.058
7	0.071	0.061	0.010
5	0.227	0.216	0.011
9	0.252	0.210	0.042
Total 125	Av. 0.2045	0.1713	0.0332

Table IV. Heavy Smoke Fumigations in a Smelter Area

Date and Time[a] of Gas Sampling, 1946	Approximate Duration of Gas in Open Atmosphere	Temperature	Atmospheric Conditions during Exposure	SO_2 in Sulfur Contaminants
	Hours	° *C.*		%
June 27 13:50–14:22	2	30 –31.5	Sky clear and bright. Visibility about 2 miles. Odor and taste of SO_2. Calm to light S wind. Smoke coning	95.2
June 29 10:15–10:45	12	28 –29.5	Smoke layer formed at upper levels during night. Fog and calm in early A.M. Sun clearing fog at 8:25. Light SE wind. Sky clear and bright at 9:50 but smoke haze present	69.1
July 10 9:20–10:30	2–3	20 –22.5	Occasional clouds in sky. Wind light. Heavy smoke haze on ground	88.4
10:35–12:00	3–4½	22 –25	Strong SO_2 odor	74.7
July 16 10:25–10:45	1–2	21 –22.5	Clear, bright. Heavy ground smoke haze. SO_2 taste and odor. Smoke clearing with increasing wind at 10:55	98.1
July 17 9:20–10:05	4	19.5–21	Smoke formed in early A.M. above ground level. Sky clear. Very light SW wind.	92.5
July 18 9:50–10:20	2–3	26 –27	Cloudless sky. Strong SE wind. Heavy ground smoke haze. SO_2 tasted	90.3
July 20 12:30–13:42	2	25.5–28	Sky clear. Hot and sultry. Light SW wind to almost calm. Visibility in heavy smoke haze, about ¾ mile or less. Odor of SO_2 distinct	93.1
July 27 9:45–10:22	5–6	19.5–22.5	Smoke collected at upper atmospheric levels in early A.M. Sky clear, light SW wind. Heavy smoke haze. Odor of SO_2. Fumigation commenced before 9:00	81.2
July 30 8:55– 9:35	2	20 –21	Sky clear, strong NE wind bringing smoke to ground level. Heavy haze	83.8
9:50–10:20	<2	20 –22	Heavy smoke haze dissipated at 10:27	96.5
August 1 11:00–11:47	4–5	25 –28.5	Sky clear, light SE wind. At 8:10, smoke visible in compact layer to SW. No roads available. Remained at location until heavy smoke drifted in	83.6
August 5 9:45–10:10	2–3	21 –22	Sky clear, almost calm. No smoke at 8:05. Smoke haze appeared at location about 9:30	88.0
August 14 10:20–11:10	5–6	19 –20.5	Smoke in layer above ground in early A.M. Sky clear. Light ground haze about 9:00 without appreciable smoke. Light SW wind. Smoke moving in about 9:40. Dense haze at 10:20, clearing about 11:30	82.2
August 23 10:00–11:55	2–4	15 –17	Light overcast sky. Dense smoke haze over area. Light N to NE winds. Cloudy and cool	88.8

[a] All times mentioned in this and subsequent tables are Eastern Daylight Saving time.

Sulfur dioxide, after release to the atmosphere, undergoes a slow oxidation to sulfur trioxide and sulfuric acid. The reaction is catalyzed by sunlight and fine dust particles, especially by minute metallic oxide particles found in smelter smoke. These sulfur components, especially sulfuric acid mist, give rise to a tremendous number of condensation nuclei in the air. Such nuclei, because of their hygroscopic nature, can transform the water vapor in the air to minute droplets which vary in size and play an important role in promoting smog conditions. It is probable that the persistent haze and lowered visibility noticeable in fumigations are due to the presence of hygroscopic sulfuric acid nuclei.

The prevailing atmospheric conditions, the approximate duration of the smoke in the open atmosphere prior to sampling, and the average percentage of sulfur dioxide in the sulfur contaminants during various smoke visitations are shown in Tables IV, V, and VI. The most important factors governing the extent of oxidation of sulfur dioxide in the open atmosphere are probably the duration of exposure and the number of nuclei or metallic oxide particles that act catalytically per unit volume of smoke. Although no sampling was attempted at night, there is evidence from data in Tables IV to VI that oxidation in the open air may take place at night as well as in sunlight. High relative humidity may promote oxidation by solution of sulfur dioxide by minute water droplets which would be deposited on solid particles. It is safe to assume that smelter smoke contains an abundance of active catalytic dust particles and consequently the dominant factor in extent of oxidation may well be the duration of the smelter gas in the open atmosphere before it is dissipated by wind and other meteorological conditions. The oxidation products,

Table V. Medium Smoke Fumigations in a Smelter Area

Date and Time of Gas Sampling, 1946	Approximate Duration of Gas in Open Atmosphere	Temperature	Atmospheric Conditions during Exposure	SO_2 in Sulfur Contaminants
	Hours	° *C.*		%
June 27 10:00–11:00	9	23 –25	Smoke layer formed during night. Atmosphere in neutral stability to moderate inversion. Calm at 7:45, no smoke at ground levels until about 9:30. Sampling in definite smoke haze which obscured hills to north. Sky clear and bright. Smoke dispersed rapidly after 11:00 by light SW wind	92.3
June 29 11:12–11:45	12	31 –32	Smoke layer formed during night at upper atmospheric levels. Sky clear and bright. Pronounced smoke haze. Odor and taste of SO_2 noted for short intervals	65.0
12:05–12:40	13	31 –33	Lapse conditions	79.8
July 4 10:10–13:25	12–15	24 –28	Smoke layer formed during night in neutral atmosphere. Definite smoke haze at time of sampling. Wind light	75.1
July 10 14:40–15:19	2–3	28 –30	Sampling in smoke haze. Occasional clouds in sky. Fumigation shifted to north by brisk SW wind	89.4
16:00–16:40	3–4	26 –29	Sampling at new location. In heavy haze. Odor and taste of SO_2 noted	84.7
July 13 10:00–11:10	3–4	19.5–22.5	Clear, bright sky. In smoke haze, calm to light breeze	79.9

(*Continued on next page*)

Table V. Medium Smoke Fumigations in a Smelter Area (*Cont'd.*)

Date and Time of Gas Sampling, 1946	Approximate Duration of Gas in Open Atmosphere	Temperature	Atmospheric Conditions during Exposure	SO_2 in Sulfur Contaminants
	Hours	° *C.*		%
July 13				
13:10–15:55	2–3	25 –28	New location. Smoke haze moving into valley. Clear, bright sky. Ground smoke lifted with increasing SE wind	95.0
July 17				
10:32–11:00	2–3	21.5–22.5	Clear, strong SW wind	86.3
11:15–11:35		23 –24	Smoke haze moving along surface	81.2
July 18				
11:43–12:25	5	29 –30	Clear sky, strong SW wind. Smoke haze spreading on all sides	75.0
July 22				
11:55–12:42	4	25 –27	Cloudy, sky overcast. Calm. Heavy smoke haze moved in to location. Smoke present since about 8:30	75.0
14:07–14:40	2–3	26 –29	Sky clear. Hot. Light SE wind. Smoke haze on all sides. Heavy cumulus clouds forming at 14:40	89.0
July 24				
10:14–11:20	3	22.5–24	Clear, light cumulus clouds. Strong W wind. Ground smoke moving in and out	79.7
July 30				
10:46–11:40	<5	21 –23	Sky clear, strong NE wind. Sampling in smoke haze	94.5
August 5				
10:17–11:08	3–4	22 –24	Sky clear. Density of smoke haze increasing, and decreasing with wind speed	73.7
11:15–12:14		24 –26		78.0
August 8				
10:05–10:50	3–4	25 –26	Sky clear. SSE wind. Smoke coning to ground level. Dense haze. Ground smoke present since 9:17	83.0
August 9				
9:50–11:17	3–4	19 –22	Heavy fog at 8:20. Very light S to SW wind. Visibility about 300 yards at 10:40, odor of SO_2, almost calm. Fog and smoke clearing at 11:22 with increasing wind speed	97.8
August 12				
9:50–10:30	10–12	16 –17.5	Smoke accumulated in layer overnight, about 500 to 800 feet above ground. Strato-cumulus overcast. Light NW wind. Dense haze	62.7
11:15–12:08		16 –18.5	Low clouds forming about 12:00	77.0
August 22				
10:15–10:50	3–4	15 –16	Cloudy. Light NW wind which increased in velocity at 10:45. Odor of SO_2 at 10:35	77.6

therefore, accumulate during prolonged periods of temperature inversions.

Investigations by the U. S. Public Health Service, following the smog disaster at Donora, Pa., indicate in air analyses that average values for sulfur dioxide (iodometrically) were lowest, for total sulfur (turbidimetrically) were intermediate, and those recorded at the same time by a Thomas automatic unit were highest, all results being expressed as parts per million of sulfur dioxide by volume (*18*, pp. 122–3).

The analytical methods described in this paper are important in assessing the relative toxicity of smoke visitations to vegetation, and the effects on materials of construction and public health. Sulfur dioxide is more injurious to vegetation than sulfuric acid in equivalent concentrations. The permissible ground level of sulfur dioxide concentration has been set at 0.30 p.p.m. during the growing season and 0.50 p.p.m. during the nongrowing season for a regime established in the case of a smelter at Trail, B. C. (*2*). Scientific investigation has shown that sensitive plants may undergo treatment with sulfur dioxide for prolonged periods in the range of 0.10 to 0.20 p.p.m. without any adverse effects on growth and photosynthesis. The rate of photosynthesis may, however, be lowered by fumigations with concentrations higher than about 0.40 p.p.m. If, however, the duration is short and not prolonged to the point of visible leaf destruction, the effect on assimilation is only temporary (*6*).

Sulfuric acid mist is more toxic to human health than sulfur dioxide. The permissible concentrations for man for prolonged exposure have been set at about 1 p.p.m. for sulfur trioxide, 2 to 10 p.p.m. for sulfuric acid, and about 10 p.p.m. for sulfur dioxide.

Under exceptional conditions the sulfuric acid content of the smoke in the Sudbury area was found to range as high as 25 to 35% of the total sulfur contaminants.

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Table VI. Mild Smoke Fumigations in a Smelter Area

Date and Time of Gas Sampling, 1946	Approximate Duration of Gas in Open Atmosphere	Temperature	Atmospheric Conditions during Exposure	SO_2 in Sulfur Contaminants
	Hours	° *C.*		%
July 2				
8:20–10:47	1–3	16 –24	Sunny and cloudless. Mild lapse conditions, smoke coning. Smoke haze increasing and decreasing	85.6
13:12–14:00	4	23 –25	Cumulus overcast, high humidity, some smoke haze present. Rain at end of sampling period. Wind light	75.7
July 3				
9:20–10:50	5–6	18.5–21	Bright sunshine. Light haze in valley. Sky cloudless	81.5
July 8				
10:50–11:30	4	22.5–24	Cloudy, low overcast, sunlight breaking through clouds about 11:30. Slight wind	82.2
July 13				
8:00– 9:40	1–3	17 –21.5	Sky clear. Smoke coning. Calm to light breeze	93.1
11:14–11:57	2–3	22 –26.5		92.0
July 16				
9:30–10:00	3–4	18.5–19	Clear. Slight ground haze. Samples represent latter part of mild early morning fumigation	77.8
August 8				
14:00–15:16	3–4	29 –31	Sky clear. Strong SW wind, gusty	81.6
August 15				
11:00–11:48	5–6	21.5–22	Sky overcast. Light SW wind	85.5
August 21				
10:35–11:10	10–12	17 –18	Low overcast; Light SE wind. Rain from 8:40 to 10:15. Smoke stream in built-up layer above ground level during night. Rain at 11:45	71.5
14:10–14:45	...	16	Low cloud layer. Smoke stream overhead and disappearing into cumulo-stratus layer. Raining at 14:45	85.9
August 22				
9:00– 9:30	2	17	Clear, light NW wind. Heavy cumulus clouds forming after 9:30	95.1
14:10–15:00	5–6	20 –21.5	Sky clear. Variable N to NE winds. Light smoke haze	83.3

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Carius Iodometric Microdetermination of Iodine in Organic Compounds

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A method is described for the determination of iodine in 5- to 10-mg. samples of organic compounds containing not more than 4 mg. of iodine. Certain samples in aqueous solution also can be analyzed by the method. The method combines the well known and highly respected Carius digestion with a simple modification of the widely used Winkler iodometric titration. Adequate provision is made for elimination of nitrite interference. The method is characterized by simple techniques, specificity, a favorable volumetric factor, an excellent end point, and short working time per sample.

THE classical Carius method is seldom used for the determination of iodine in organic compounds because of the unfavorable gravimetric factor, the interference caused by other halogens, and the impurity of the silver iodide precipitate (*7*, *18*). The silver normally present in the Carius digest interferes with the measurement of the iodine by the excellent iodometric method proposed by Winkler (*20*), modified by Burgarszky and Horvath (*2*), Leipert (*8*), and many others, wherein the iodine originally present in the sample is oxidized and the iodate thus formed is allowed to react with excess iodide to form free iodine according to the reaction

$$IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O$$

Most analysts, therefore, have adopted the method of either burning the sample in a stream of oxygen in a quartz tube (*11*, p. 172; *12*, p. 94; *17*) or decomposing it with sodium peroxide in the all-metal bomb (*4*) in order to destroy the organic matter and convert the iodine to a form susceptible to iodometric measurement. Such methods are often unsatisfactory because of long working time, incomplete removal of the iodine from ash, reaction of possible constituents of the sample with quartz combustion tubes, and inability to decompose samples that are in aqueous solution. Because the Carius digestion has none of these disadvantages, a method permitting its use with subsequent iodometric measurement of the iodine would have an advantage.

Doering (*3*) proposed a macromethod for the determination of iodine in organic compounds, in which the sample was heated in a sealed glass tube with mercuric nitrate instead of silver nitrate, as in the Carius method. Mercury, like silver, serves to render the iodine nonvolatile and has the added advantage that it does not interfere in any way with the oxidation of the iodine and its measurement by the Winkler iodometric method. Neither the method of Doering nor the micromodification proposed by Weygand and Werner (*19*) appears to be well known in this country.

Chlorine used by Doering in the Winkler method to oxidize the iodide to iodate also oxidizes nitrites and/or other interfering materials in the Carius digest which are capable of liberating iodine from acidified iodide solutions. The use of chlorine as oxidant in the iodometric method for iodine has two serious disadvantages: Bromide, if present, may interfere with the determination of iodine (*5*, *8*, *9*, *16*), and it is comparatively difficult to remove excess chlorine quantitatively without loss of iodate (*6*, *9*). Incomplete removal of the chlorine leads to high results.

Bromine is far superior to chlorine as the oxidant for this method, because interference from other halogens is not encountered, bromine is more stable than the sodium hypochlorite solutions usually used (*8*) and is free from blank (*2*), and the excess bromine can be easily and quickly removed at room temperature without loss of iodate. For these reasons bromine has almost completely supplanted chlorine as oxidant for the iodometric determination of iodine. Bromine, however, cannot be substituted for chlorine in the Doering method, because it is not capable of completely oxidizing the nitrite formed during the Carius digestion (*5*, *8*, *9*).

This paper presents a micromethod for the determination of iodine in organic compounds which combines the Carius digestion and the iodometric determination of iodine. Bromine is used as the oxidant and alkaline sulfite–sulfamic acid reagent is employed to remove nitrites. The Carius digestion is applicable to nearly all types of compounds and the reagents are few and nearly free from blank; there is no possibility of loss of iodine

through volatilization or incomplete extraction from ash, and samples containing alkali metals do not damage the combustion tubes; the iodometric method used to measure the iodine is one of the most exact and precise volumetric methods known; the volumetric factor is favorable; the working time for both digestion and titration is favorable; and the techniques required are simple and well known and the reagents are essentially the same as those commonly used in many laboratories for the Leipert iodometric method for iodine and the Vieböck method for methoxyl (*11*, pp. 172 and 239; *12*).

APPARATUS AND REAGENTS

Carius tubes are made from borosilicate glass tubing 0.5 inch in outside diameter, $^3/_{32}$-inch wall, and approximately 7 inches long. This tubing is also sold as Pyrex Brand high pressure gage glass, and is usually available from boiler supply or mill supply companies.

Carius Furnace. Any suitable tube furnace capable of heating the sealed combustion tubes to 300° C.

Nitric Acid–Mercuric Nitrate Reagent. Dissolve 20 grams of reagent grade mercuric nitrate [$Hg(NO_3)_2.xH_2O$] in 100 ml. of nitric acid, conforming to AMERICAN CHEMICAL SOCIETY specifications, specific gravity 1.42. (The solution should assay approximately 13 grams of mercury per 100 ml.)

Alkaline Sulfite–Sulfamic Acid Reagent. Dissolve 10 grams of sodium sulfite, A.C.S., and 5 grams of pure aminosulfonic acid (sulfamic acid) in 300 ml. of 15% w./v. cool sodium hydroxide. The reagent is stable at least one month.

Sodium acetate (trihydrate), A.C.S., 20% aqueous solution.

Solution of sodium acetate (trihydrate), A.C.S., in glacial acetic acid, 10%.

Bromine, A.C.S., free from iodine (traces of iodine may be removed from the bromine by shaking it cautiously in a separatory funnel with several small portions of water).

Formic acid, A.C.S., 90%.

Potassium iodide, A.C.S., granulated, free from iodate.

Sulfuric Acid, Dilute. Add 1 volume of concentrated A.C.S. sulfuric acid to 9 volumes of distilled water.

Sodium thiosulfate, 0.01 *N*; is standardized against potassium biiodate under the conditions of the method, using all the reagents.

Starch Indicator. Dissolve approximately 5 grams of 20% amylose (G. Frederick Smith Chemical Company) in 100 ml. of boiling water and allow to cool to room temperature. Filter through glass wool and add a few drops of mercury as preservative. The end point is sharper with the amylose indicator than with the usual soluble-starch indicator, but the latter may be used.

Potassium biiodate, 0.0008 *M* (0.3249 gram of the pure dry salt per liter), for standardizing the thiosulfate.

PROCEDURE

Weigh a 5- to 10-mg. sample containing not more than 4 mg. of iodine into a Carius tube and add 0.3 ml. of nitric acid–mercuric nitrate reagent. Seal the tube as usual and digest 3 hours at 300° C. Allow to cool to room temperature in the furnace and then heat the tip of the tube with a soft flame to drive out the condensed acid. Cool the lower half of the tube in ice water. Apply a sharp, small flame to the capillary until it opens as a result of slight internal pressure. Make a file scratch near the constriction and open the tube with a hot glass rod as usual.

Wash the contents of the tube into a 125-ml. iodine flask containing 3 ml. of alkaline sulfite–sulfamic acid reagent and 5 ml. of aqueous sodium acetate solution. Use approximately 20 ml. of water to wash out the tube and the tip. Add 5 ml. of glacial acetic acid–sodium acetate solution and mix well. Add bromine (approximately 0.12 ml.) until the solution is clear and a strong yellow-brown color remains after thorough shaking. Allow to stand at least 2 minutes to permit complete oxidation, then add formic acid (approximately 0.25 ml.) down the side of the flask. Shake the stoppered flask cautiously until no more pressure develops. If the solution is not perfectly colorless, add a few more drops of formic acid. Wash down the neck of the flask and draw a current of air over the liquid (*14*) to sweep all bromine fumes from the flask. Add 0.5 gram of potassium iodide and 4.5 ml. of the dilute sulfuric acid, and swirl the stoppered flask gently to dissolve the iodide. Allow to stand 5 minutes; then titrate the liberated iodine rapidly with 0.01 *N* sodium thiosulfate to a pale yellow color, add 2 drops of the amylose indicator solution, and continue the titration to a colorless end point.

A blank determination should be made using all reagents; however, the blank need not be digested. The blank titration is usually about 0.02 ml. of 0.01 *N* sodium thiosulfate.

The calculations are made as follows:

$$\frac{\text{Net ml. of 0.01 } N \text{ } Na_2S_2O_3 \times 0.21153 \times 100}{\text{sample wt. (mg.)}} = \%I$$

RESULTS

National Bureau of Standards No. 145 2-iodobenzoic acid, pure potassium iodobenzoate, and a group of commercial organic chemicals of unknown purity containing a variety of elements and functional groups were analyzed by this method and by the Grote method as described by Sundberg and Royer (*17*), modified to give a more dilute acid solution for the liberation of the iodine.

For the eleven samples analyzed by both methods (Table I) the difference between the high and low value for the Carius method averaged 0.14% and for the Grote method, 0.15%. Results by the Carius method averaged higher than did those by the Grote method for five of the samples. The average values obtained by the two methods agreed within 0.1% for four of the samples and in no case was the difference more than 0.2%. The average difference between results by the two methods was 0.12% (equivalent to 0.03 ml. of 0.01 *N* sodium thiosulfate for a 5-mg. sample). Because of the high percentage of iodine in the samples, this discrepancy amounted to an average difference of only 2.3 parts per thousand.

These data show that the accuracy and precision of the proposed method are good.

DISCUSSION OF METHOD

All Carius microtubes used in this laboratory are made from heavy-walled borosilicate glass tubing 0.5 inch in outside diameter. As a safety precaution, commercial thin-walled Carius tubes should not be used for this method. Explosions with the heavy-walled tubes are exceedingly rare and no such tube has ever exploded in this laboratory after it was cool. The tubes may be re-used as long as they are of sufficient length. Dried samples may be conveniently placed in the tubes with A.C.S. specification (*15*) capped weighing tubes. Materials that react with cold

Table I. Recovery of Iodine from Organic Compounds

Sample	Carius-Iodometric Method		Grote Method	
	Av. %	Replicates %	Av. %	Replicates %
2-Iodobenzoic acid, N.B.S. No. 145	51.09[a]	...	51.15	51.18, 51.18, 51.10
o-Iodophenol	57.54	57.62, 57.55, 57.44	57.36	57.45, 57.37, 57.27
p-Chloroiodobenzene	53.05	53.12, 53.02, 53.00	52.91	52.92, 52.90
p-Bromoiodobenzene	44.53	44.60, 44.52, 44.46	44.34	44.45, 44.33, 44.23
p-Diiodobenzene	76.64	76.71, 76.61, 76.61	76.75	76.85, 76.76, 76.63
p-Nitroiodobenzene	50.75	50.77, 50.77, 50.71	50.83	50.88, 50.82, 50.80, 50.80
p-Iodoaniline	58.67	58.76, 58.73, 58.71, 58.47	58.58	58.78, 58.55, 58.42
β-Iodopropionic acid	63.08	63.17, 63.04, 63.02	63.24	63.29, 63.28, 63.26, 63.11
Hexamethylenetetramine ethiodide	42.74	42.80, 42.74, 42.68	42.89	42.91, 42.88, 42.87
7-Iodo-8-hydroxyquinoline-5-sulfonic acid	35.70	35.76, 35.74, 35.70, 35.61	35.65	35.72, 35.67, 35.55
Potassium iodobenzoate	44.29	44.32, 44.25	[b]	
3,5-Diiodo-L-tyrosine (air-dry sample)	57.87	57.88, 57.86, 57.86	57.99	58.04, 57.97, 57.96
3,5-Diiodo-L-tyrosine (lyophilized in Carius tube)	57.91	57.99, 57.91, 57.84	...	...

[a] Average of 12 analyses: maximum, 51.17%; minimum, 50.99%; standard deviation, 0.057%. Theory, 51.17% I.

[b] Not susceptible to analysis by Grote method. Theory, 44.36% I.

nitric acid should be kept from contact with the acid until the tube is sealed; either the sample or the acid may be introduced into the tube in a small, thin-walled vial. In some cases aqueous solutions of organic compounds or biological preparations may be aliquoted into the tube, shell-frozen in a dry ice–acetone bath, and vacuum-dried from the frozen state (lyophilized).

All digestions made in this study were carried out at 300° C. for 3 hours. Three hundred degrees is the maximum temperature usually recommended for the Carius digestion and the 3 hours' duration of heating is considerably greater than the 1-hour period recommended by Niederl *et al.* (*10; 11*, p. 156). Other workers have recommended longer times, and for certain unusual samples extended digestions may be necessary. No study was made to determine whether the digestions could be carried out satisfactorily at lower temperature or for a shorter time, or whether fuming nitric acid could be used.

The application of this method to the determination of traces of iodine in organic materials was not attempted, for sample weights beyond the scope of the method would probably be required. The method described here has been used, however, for 12- to 15-mg. samples of iodinated proteins containing as little as 0.5% iodine.

The alkaline sulfite–sulfamic acid reagent is used to neutralize the nitric acid and to eliminate the nitrites formed during the digestion. Nitrite must be removed, because it will liberate free iodine from an acid iodide solution. The chlorine used as oxidant by Doering (*3*) completely oxidizes the nitrites, but the bromine used in this method will not completely perform the oxidation (*5, 9*). Other workers have destroyed traces of nitrites formed during dry combustion of nitrogenous substances with such reagents as ammonium chloride, bisulfite, urea, and sodium azide (*5*). The authors have found that the combination of sulfite and sulfamic acid used as described herein is entirely effective in removing the relatively large amount of nitrites formed during the digestion. The other reagents, particularly sodium azide, could probably be used for this purpose; however, Baumgarten and Marggraff (*1*) report that sulfamic acid is more effective than sodium azide.

Bromination and removal of the excess bromine should be carried out at room temperature, because elevated temperatures tend to displace the equilibrium

$$I_2 + 5Br_2 + 6H_2O \rightleftharpoons 2IO_3^- + 12H^+ + 10Br^-$$

toward the left (*6, 13*). For the same reason, the iodide and acid should be added to form the iodine soon after the excess bromine is discharged.

Aside from weighing, the working time per sample is about 30 to 35 minutes.

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Carius Iodometric Microdetermination of Bromine in Organic Compounds

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THE classical Carius method offers the simplest and most direct means for the determination of bromine in organic compounds. However, the gravimetric factor is rather unfavorable, chlorine and iodine interfere, and, because the bromine is measured gravimetrically, the procedure is time-consuming. Although argentometric, acidimetric, and iodometric methods have been used for the volumetric estimation of bromine following certain wet and dry combustions of the sample, no simple volumetric method employing the favored Carius digestion has been proposed for the determination of this halogen. The iodometric measurement of bromine, which is based on the reactions

$$Br^- + 3HOCl \longrightarrow BrO_3^- + 3H^+ + 3Cl^-$$

and

$$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3H_2O + 3I_2$$

is preferred over other volumetric methods (*4*) because of freedom from interference by chloride and nitrogen, the sharpness of the end point, and the favorable volumetric factor.

The work reported herein was undertaken to develop a simple method that would combine the excellent Carius digestion and the preferred iodometric estimation of the bromine.

EXPERIMENTAL

Silver is commonly used to fix in the nonvolatile state the halogen formed during the Carius digestion. Mercury has been used for this same purpose by Doering (*2*), Weygand and Werner (*6*), and White and Secor (*7*) in methods for the Carius-iodometric determination of iodine. Silver and mercury interfere with the quantitative oxidation of bromide to bromate and/or with the subsequent removal of the excess oxidant. No simple way could be found to eliminate this interference. No other chemical means was found which would render nonvolatile the halogen in the digest and would not interfere with the subsequent operations.

The vapor pressures of bromine and of hydrobromic acid are

The excellent Carius digestion has been combined with the iodometric measurement of bromine to produce a simple method for the determination of this halogen in organic compounds. The method is novel in that low temperature instead of chemical combination is used to render the bromine in the digest nonvolatile. Chloride and nitrogen do not interfere, but iodine is quantitatively determined. The method is characterized by simple technique, a very favorable volumetric factor, a good end point, and short working time per sample.

about 0.05 and 500 mm. of mercury, respectively, at −75° C. (*5*)—a temperature which is easily obtained in a dry ice–alcohol bath. Therefore, no measurable loss of bromine should occur if the Carius digestion is carried out under conditions which preclude the formation of hydrobromic acid and if the digestion tube is opened at the temperature of dry ice–alcohol and the digest is immediately made alkaline. When *o*-bromobenzoic acid was digested with nitric acid, very slight traces of bromine-containing material (presumably hydrobromic acid) could be detected in gases escaping when the tube was opened at −75° C. However, no bromine could be detected in these gases when a few milligrams of sodium chloride were added to the mixture prior to digestion.

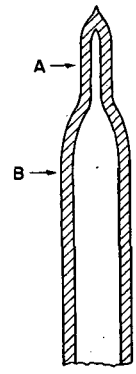

Figure 1. Sealed Carius Tube

The pressure within the Carius tubes at room temperature is not sufficient to cause any hazard in handling the heavy-walled tubes used and, at −75° C., the pressure is so very slight that they may be opened as described below without fear of explosion.

The phosphate buffer and Clorox, a commercial bleaching agent, used by Alicino, Crickenberger, and Reynolds (*1*) were found to be the simplest reagents for the quantitative oxidation of bromide to bromate. Prior to the appearance of their paper the authors had used sodium hypochlorite with borate buffer (*4*) and also calcium hypochlorite with calcium carbonate buffer (*3*).

A careful study was made of methods for standardizing the sodium thiosulfate for use in this determination.

Five-, 10-, and 15-ml. aliquots of 0.0025 *M* potassium bromide, 0.0025 *M* potassium bromate, and 0.00125 *M* potassium biiodate were added in duplicate to digested and to undigested blanks. The oxidation, removal of excess oxidizing agent, liberation of iodine, and titration were then carried out according to the procedure used for digested samples. For this purpose thiosulfate was prepared daily by careful dilution of standardized 0.1 *N* reagent with boiled, cooled redistilled water. The apparent normality of the sodium thiosulfate was the same (within experimental error) for the three standards, for the three levels of iodine titrated, and for aliquots added to either the digested or the undigested blanks. The normality as determined by the 36 titrations was 0.01492 ± 0.000025, which compares favorably with 0.01491 *N*, the value calculated.

The quantitative retention of bromine and iodine in a Carius digest prepared from only nitric acid, sodium chloride, and sample suggests the possibility of using this excellent method of digestion in conjunction with potentiometric or amperometric methods for measuring these halogens.

APPARATUS AND REAGENTS

Carius tubes and Carius furnace are the same as those used for determination of iodine (*7*).

Dry ice–alcohol bath.

Hypodermic syringe, Luer, 5-ml., with needle.

Dropper, calibrated to deliver 0.30 ± 0.02 ml.

Nitric acid, A.C.S., specific gravity 1.42.

Sodium chloride, A.C.S.

Sodium hydroxide, A.C.S., 5% w./v. in water.

Sodium dihydrogen phosphate, reagent grade, 20% w./w. in water.

Clorox, commercial bleaching solution, 5.25% sodium hypochlorite.

Sodium formate, reagent, 50% w./w. in water, filtered if necessary.

Sulfuric acid, 9 *N*.

Ammonium molybdate, reagent, 5% w./v. in water.

Potassium iodide, A.C.S., granulated, free from iodate.

Sodium thiosulfate, 0.015 *N*, prepared daily by careful dilution of 0.1 *N* standardized reagent with boiled, cooled, redistilled water or by standardization of approximately 0.015 *N* sodium thiosulfate against 0.0025 *M* potassium bromide, 0.0025 *M* potassium bromate, or 0.00125 *M* potassium biiodate. The salts used as primary standards should be especially purified and dried.

Starch Indicator. Dissolve 5 grams of 20% amylose (G. Frederick Smith Chemical Company) in 100 ml. of boiling water and allow to cool to room temperature. Filter through glass wool and add a few drops of mercury as preservative.

PROCEDURE

Weigh a 5- to 8-mg. sample containing not more than 4 mg. of bromine into a Carius tube and add about 10 mg. of sodium chloride and 0.30 ml. of nitric acid. Using a gas-oxygen torch, seal the tube with a long, slim tip as shown in Figure 1. Digest 3 hours at 300° C. (*7*), allow to cool to room temperature in the furnace, and then heat the tip of the tube with a soft flame to drive out the condensed acid. Thoroughly cool the lower inch or two of the tube in the dry ice–alcohol bath to freeze the bromine in the bottom, and finally immerse the entire tube in the bath for a few minutes. Remove the tube from the bath, quickly wrap it in a towel, and make a file scratch at *A*, Figure 1. Hold the tube in an inclined position with the scratch resting on a sharp edge and break off the tip by striking it with the file. Immediately add 4.2 ml. of 5% sodium hydroxide with the syringe and thoroughly mix the contents of the tube by shaking or by resealing the tip of the tube and inverting. Make a mark around the tube at *B* with a Griffin-type glass tubing cutter or with a file and crack it with a hot glass rod as usual. Break portion *A-B* of the tube

Table I. Bromine Content of Organic Compounds

Compound	Bromine, % Carius-Iodometric	Theoretical
p-Nitrobromobenzene	39.58 39.77	39.56
p-Chlorobromobenzene	41.53 41.50	41.74
p-Bromoiodobenzene	28.12[a] 27.99	28.25
5,7-Dibromo-8-hydroxyquinoline	52.80 53.10	52.76
2,6-Dibromoquinonechloroimide	53.38 53.41	53.39
3,5-Dibromopyridine	67.50 67.22	67.47
p-Bromoacetanilide	37.25 37.27	37.33
p-Bromophenol	46.01 46.00	46.19
o-Bromobenzoic acid	39.53[b]	39.75

[a] Calculated from determinations on portions of same material by present method and Carius-iodometric method for iodine (*7*).

[b] Average of 24 determinations; highest, 39.74%; lowest, 39.35%; standard deviation, 0.097%.

into a 125-ml. iodine flask containing 5 ml. of Clorox solution. Transfer the contents of the tube to the flask with 25 to 30 ml. of distilled water and add 5 ml. of the phosphate buffer solution. Heat the solution just to boiling on a hot plate adjusted to bring it to an incipient boil in 8 to 10 minutes. Remove the flask from the hot plate, immediately add 3 ml. of the sodium formate solution, and swirl gently. Allow to stand 3 to 4 minutes, then cool to room temperature in running cold water. Add 5 ml. of 9 *N* sulfuric acid, 0.5 gram of potassium iodide, and 2 drops of the ammonium molybdate and titrate rapidly with 0.015 *N* sodium thiosulfate. Add 2 drops of amylose (or other starch indicator) just before reaching the colorless end point.

A blank determination should be made with all reagents; however, the blank need not be digested. The blank value varied from 0.04 to 0.2 ml. of 0.015 *N* thiosulfate, depending on the bottle of Clorox used.

The calculations are made as follows:

$$\% \text{ Br} = \frac{\text{net ml. of 0.015 } N \text{ thiosulfate} \times \frac{79.916}{6} \times 0.015 \times 100}{\text{sample weight (mg.)}}$$

In a large group of samples the working time, aside from weighing, is about 25 minutes per determination.

The data in Table I show satisfactory precision and accuracy for a group of organic bromine compounds containing chlorine, iodine, and nitrogen. Unreported data indicate that iodine is quantitatively determined by the method. Therefore, it is an interfering element. The iodine may, however, be determined in a separate portion of the sample by the Carius-iodometric method for iodine (7) and the bromine content of the sample may then be calculated from the results of the analyses by the two methods.

The method has not been applied to biological materials. The lyophilization technique described previously (7) should be applicable to many such samples.

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Direct Microdetermination of Oxygen in Organic Compounds

Comparison between Unterzaucher and ter Meulen Methods

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A comparison of the ter Meulen, Liebig, and Unterzaucher methods for determining oxygen in organic compounds is presented. The ter Meulen method proved unsatisfactory for nitrogen compounds because the alkali hydroxide used to absorb water selectively and exclude ammonia was found inefficient for complete retention of the water formed. Oxygen obtained by Liebig's method has ascribed to the oxygen value the sum of all the errors of carbon and hydrogen evaluation. Moreover, the method yields inaccurate results on samples leaving a mineral ash if components of the residue undergo change in weight during ashing. The Unterzaucher method, although generally satisfactory, gives incorrect results on organic products containing inorganic carbonates or oxides. Pyrolysis of sulfur compounds produces hydrogen sulfide, carbon disulfide, and carbonyl sulfide. An Ascarite scrubber will not retain carbon disulfide nor carbonyl sulfide. These sulfides should be withheld by a liquid nitrogen trap; otherwise, both compounds will release iodine from iodine pentoxide, causing erroneous results.

THE development of an accurate method for the determination of oxygen has become of increasing importance in connection with petroleum research, particularly for the detection and determination of small amounts of oxygenated compounds in petroleum fractions. A direct method should solve this problem and would have obvious advantages over the usual procedure of reporting the amount of oxygen in a compound as the difference between 100% and the percentage sum of all other determinations.

As Elving and Ligett (4) have pointed out, the determination by difference places the sum of all errors on oxygen and eliminates the possibility of checking the analysis by totaling the determined constituents. This error attains greater relative significance when applied to compounds containing low amounts of oxygen. Aluise *et al.* (2) have indeed shown that more precise and accurate results are obtained by the direct determination (Unterzaucher's method). This fact has been confirmed in these laboratories. A direct determination would, in addition to its accuracy, effect considerable saving in time.

The very complete review of the literature by Elving and Ligett (4), who have critically examined the available methods for the direct determination of oxygen, shows that the most important of the techniques suggested have been those based on complete oxidation of the compound with a measurement of the oxygen consumed, catalytic hydrogenation to form water, and thermal decomposition over carbon to form carbon monoxide. Of these techniques the Unterzaucher modification of the Schutze method (thermal decomposition over carbon) and the catalytic hydrogenation method of ter Meulen have been investigated by the authors. The Unterzaucher and Liebig methods have also been compared.

Table I. Oxygen Determination by Unterzaucher Method

Sample	Oxygen Found, % Liquid nitrogen trap	Ascarite scrubber	% Oxygen Theoretical
s-Benzylthiuronium chloride	0.054	6.70	0.00
	0.063	7.24	
		3.10	
	Av. 0.059	5.68	
p-Dichlorobenzene	0.136	0.118	0.00
	0.138	0.108	
	Av. 0.137	0.113	
N,*n*-Butyl benzenesulfonamide	15.04	15.74	15.00
	14.96	16.38	
	Av. 15.00	16.06	
2-Thiobarbituric acid	22.11	23.55	22.19
	22.00	25.18	
		23.85	
	Av. 22.05	24.19	

UNTERZAUCHER METHOD

In this method the sample is vaporized in a stream of nitrogen and passed over pelleted carbon heated to 1120° C. in a quartz reaction tube. At this temperature the oxygen is combined with the carbon quantitatively to form carbon monoxide according to the familiar water gas equations. The carbon monoxide is swept by nitrogen over pure iodine pentoxide heated to 125° C. and is thus converted to the dioxide. Simultaneously, the iodine pentoxide is reduced to elemental iodine which, after oxidation to iodate and subsequent reduction to free iodine, is determined by titration with a standard solution of 0.02 *N* sodium thiosulfate.

The procedure and the apparatus used are essentially those of Aluise *et al.* (*2*); a sketch of the apparatus is shown in Figure 1.

One significant change in the apparatus is the insertion of a liquid nitrogen trap to remove neutral gases originating from sulfur compounds in the sample. Such nonacidic gases are not retained by Ascarite or the usual alkali scrubbers. Walton *et al.* (*8*) made use of a similar trap containing liquid air for the retention of ethylene and acidic compounds.

The results of analysis of pure compounds both with the liquid nitrogen trap and with an Ascarite scrubber are presented in Table I; while the number of compounds studied is not extensive, it is strongly indicated that the liquid nitrogen trap is preferable to the Ascarite scrubber when the sample contains sulfur. As an illustration of this, it was found upon carrying out a qualitative analysis of the material retained in the trap, following a regular oxygen determination on several submitted samples containing oxygen and sulfur, that the retained substance was largely hydrogen sulfide with smaller amounts of carbon disulfide and carbonyl sulfide. As a result of this disclosure, several organic sulfur compounds containing oxygen were pyrolyzed under exactly the same conditions followed when running an Unterzaucher oxygen determination, except that larger amounts of sample were taken. The composition of the material retained in the liquid nitrogen trap after each run was then determined quantitatively by means of a mass spectrometer. By this method the trapped gases from an analysis of 2-thiobarbituric acid were found to consist of hydrogen sulfide 91%, carbon disulfide 4.5%, and carbonyl sulfide 4.5% by volume. Values obtained in the same manner from ditolyl sulfone were: hydrogen sulfide 93.1%, carbon disulfide 2.0%, and carbonyl sulfide 4.9% by volume. These values, however, vary considerably with the compound used, as shown in the case of toluene-sulfonic acid where the relative concentration of the trapped gases was found to be: hydrogen sulfide 80.0%, carbon disulfide 11.1%, and carbonyl sulfide 8.9% by volume.

A considerable quantity of iodine was liberated when each of these gases was passed separately through the iodine pentoxide tube. In two determinations with carbon disulfide, using samples of 4.2 and 5.26 mg., respectively, the iodine released was found to be equivalent to 117 and 118 weight % of oxygen. A similar quantitative relationship was not, however, established for either hydrogen sulfide or carbonyl sulfide.

An anomalous condition exists in the case of carbonyl sulfide. On the one hand, it liberates iodine from iodine pentoxide (if not trapped out), thus giving high oxygen results and, on the other hand, oxygen is lost whenever the compound is formed during an oxygen determination.

Larger weights (150 to 200 mg.) of sample than were ever taken for a standard Unterzaucher oxygen determination were necessary in obtaining the quantitative carbonyl sulfide data given above, and it is possible that pyrolysis of such inordinate amounts of material may have yielded quantities of the oxysulfur compound not strictly comparable to the amount obtained in a regular run. No attempt, therefore, has been made to calculate the correction for oxygen trapped as carbonyl sulfide in the regular oxygen determinations. For example, in the pyrolysis of 2-thiobarbituric acid, the amount of oxygen trapped as carbonyl sulfide as found by the mass spectrometer corresponds to 0.48% of oxygen on the original sample, an error which would be obviously out of line with the discrepancy of 0.14% when the average results shown in Table I are compared with theory. Although this discrepancy was not further investigated, it may be assumed that it was due to the loss of oxygen caused by the formation of carbonyl sulfide. Consequently, for a very accurate determination of oxygen, the amount of carbonyl sulfide condensed in the nitrogen trap should be determined and a positive

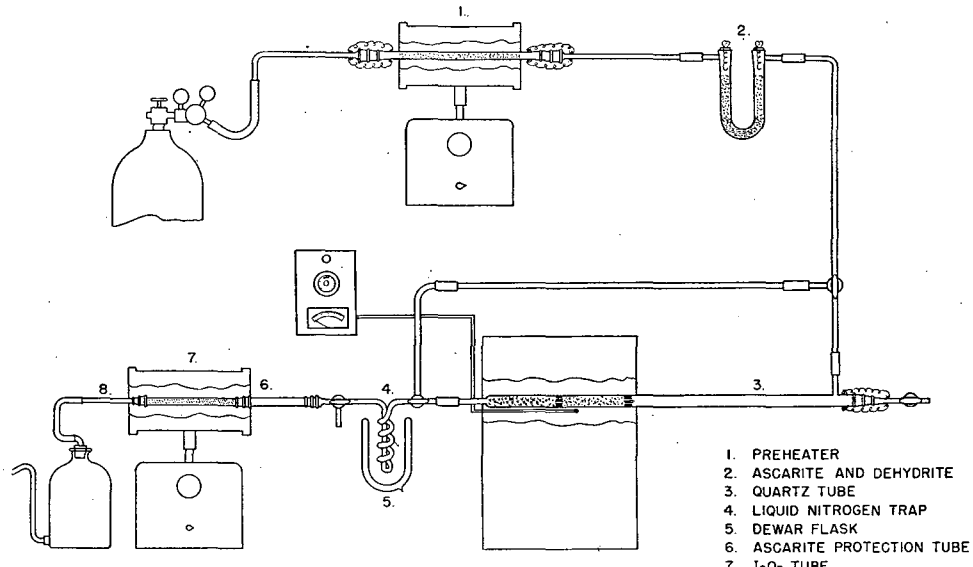

FIGURE 1
APPARATUS FOR THE DETERMINATION OF OXYGEN BY THE UNTERZAUCHER METHOD

correction made accordingly. This determination would, however, require a very accurate micromethod, because the amount collected from the weight of sample usually taken (5 to 10 mg.) would be extremely small.

A small amount of oxygen was found in those samples, the theoretical oxygen content of which is zero. It has not been determined whether this represents an absolute oxygen value because of impurities in the sample or merely the inaccuracies of the determination.

Table II. Direct Oxygen Determinations *vs.* Oxygen Calculated by Difference

Sample	Theoretical, %	Oxygen, % By Unterzaucher method	Oxygen, % By difference from combustion	Remarks
Synthetic 1	1.02	1.06	1.02	Laboratory 1
		1.07	1.04	
		1.09	1.04	
		1.12	1.13	
		Av. 1.08	1.06	
Synthetic 2	5.07	5.04	5.03	Laboratory 1
		5.08	5.09	
		5.09	5.09	
		..	5.50	
		..	5.77	
		Av. 5.07	5.29	
Crude oil fraction 1		0.48	0.04	Laboratory 1. Oxygen by oxygen type analysis = 0.38%
		0.53	0.15	
		0.49	0.05	
		..	0.02	
		Av. 0.50	0.04	
Crude oil fraction 1			0.35	Laboratory 2
			0.30	
			0.36	
			0.26	
			0.32	
Gilsonite[a]		6.40	5.88	
		6.44	6.19	
		..	5.97	
		Av. 6.42	6.01	

[a] Ash = 0.41%.

Comparative results for oxygen content by the Unterzaucher and Liebig methods are given in Table II, where it is shown that there is a considerable degree of variation in the results by difference on all samples except synthetic 1. These deviations, in fact, caused much discussion in the authors' laboratories, especially regarding the question of the presence of oxygenated compounds in the crude oil fraction. For this reason, positive confirmation was obtained by carrying out oxygen-type analysis on this sample. An infrared spectroscopic examination revealed a strong carbonyl band, thus also confirming the presence of oxygen. Data are at hand from several laboratories, reporting results of analysis for oxygen by the Liebig method on two synthetic samples and showing an amount ranging from 4.55 to 5.47% on one sample and from 0.50 to 1.59% on the other. Such wide variations, obviously, point to the need of an improved method for determining oxygen accurately.

Data are presented for the gilsonite sample having an ash content of 0.41% to warn analysts of the possibility of obtaining unreliable results by either the Liebig or Unterzaucher methods when determining organically combined oxygen in samples containing constituents that will leave a mineral ash. If the components of this residue had undergone any change in weight during the process of ashing—e.g., oxidation or decomposition—an error for organic oxygen values would be introduced when obtained by the Liebig method.

The authors' experience using the Unterzaucher method on samples from a coal gasification plant showed that the presence of inorganic oxygen compounds could cause high results for organic oxygen if these compounds are reduced or thermally decomposed. For example, it has been found in these laboratories that carbonates are decomposed and the oxides of iron and lead are at least partially reduced under the conditions of analysis imposed by this direct method. Thus, there could be an error in the Unterzaucher results on the gilsonite sample, because the composition of its inorganic constituents was not known.

The following points pertaining to reagents, apparatus, and operations are described because they have not been brought out or sufficiently emphasized in various publications on the Unterzaucher determination for oxygen.

Reagents and Apparatus. The carbon used is the Wyex compact black (J. M. Huber, Inc.) recommended by Aluise *et al.* (*2*). However, as the ash content on the authors' lot is higher than Aluise reported, the carbon is digested with 1 to 2 hydrochloric acid and washed with water. After drying, it is screened and packed as described in previous literature.

The iodine pentoxide tube is conditioned according to Aluise *et al.* (*2*), except that a longer period of conditioning may be necessary. An acceptable lot of iodine pentoxide should not yield any iodine upon passage of dry nitrogen through the compound. Several brands of this material were tested in these laboratories and the product from Eimer and Amend proved satisfactory.

The nitrogen currently used as the inert gas is the Seaford Grade nitrogen made by the Air Reduction Company. It is very low in oxygen and, in addition, contains 1% hydrogen. This hydrogen catalyzed by copper in the preheater is sufficient to combine with the last traces of oxygen, thus keeping the copper in the reduced state. The cylinder of hydrogen used by other workers to reduce the copper may thus be eliminated from the apparatus.

The furnace now in use is the Type MCF-1 Micro-Tube furnace, Catalog Item 5674, from Arthur H. Thomas Company, Philadelphia. The furnace is controlled by a proportional input controller with manual adjustment. The temperature is indicated by a platinum, platinum–13% rhodium thermocouple and pyrometer. The operation of the furnace is satisfactory, except that an auxiliary heater such as Aluise's (*1*) ring burner is needed to increase the length of the heated zone. A furnace 10 cm. longer (the present one is 21 cm. long) would be more satisfactory.

The sample heater described by Aluise (*1*) or that distributed by Arthur H. Thomas Company, Catalog Item 5679-T, is recommended. Its construction, designed especially to heat the tube evenly over its entire periphery, allows better control of the pyrolysis and prolongs the life of the tube.

A device for automatic propulsion of the sample heater is highly desirable. Either of the designs published (*2*, *7*) is satisfactory as long as the speed is about 0.3 inch (0.8 cm.) a minute.

Operation Notes. Oxygen or water vapor in the air used to burn off the deposited carbon, or oxygen from accidental leakage, will adsorb on the quartz tube. This adsorbate may be removed by heating the vaporization zone and sweeping for the usual period; this should be done daily before the commencement of operation.

As a tube ages and devitrification progresses, the blank will begin to increase rapidly from reduction of the silica in contact with the carbon; at that stage the tube should be replaced. The useful life of a quartz tube may be from 3 to 5 months. The temperature of the tube is kept near 500° C. while the apparatus is not in use, as it is reported that the rate of devitrification is increased when the tube is cooled below 300° C.

Sometimes channeling will occur in the iodine pentoxide oxidation tube, resulting in a slight loss of carbon monoxide. If this condition is suspected, a quick check may be made by using a silica gel carbon monoxide indicating tube (Mine Safety Appliances Company, Catalog No. DS-47134). The indicating tube is connected to the alkali absorption tube while a sample is being analyzed. Under proper operating conditions there should be no change (or very slight change) in the bright yellow indicating gel. A loss of carbon monoxide equivalent to 0.001 mg. of oxygen is readily detected. Tapping the iodine pentoxide tube while it is held vertically will usually remove the channels. If this does not remedy the fault, the iodine pentoxide should be replaced.

When the carbon is sintered at 500° to 600° C. prior to packing in the quartz tube, glass wool should not be used to retain the carbon; otherwise the carbon becomes contaminated with small pieces of glass and an enlarged and varying blank will result from reduction of the glass particles.

It is sometimes convenient, especially with solids of low melting point, to leave the boat near the open end of the tube during the back-sweeping period. The sweeping times have been shortened over those previously reported (*3*), so that for an average sample the elapsed time is about 35 minutes exclusive of weighing and titrating. A breakdown of the running time gives approximately 5 minutes' back-sweeping, 12 to 15 minutes' sam-

ple vaporizing, and 15 minutes' sweeping. Large or volatile samples require a longer vaporizing time but rarely as long as 20 minutes. A small, coated magnet inside the tube, and propelled by an external magnet, is used to push the boat into position for vaporizing the sample. The small magnet is returned to the end of the reaction tube before the sample is vaporized.

Elaborate steps need not be taken to ensure that all connections are glass to glass. The very low blank value of 0.08 ml. of 0.02 *N* sodium thiosulfate sometimes obtained is evidence that no appreciable diffusion takes place through the various rubber connections.

TER MEULEN METHOD

This method involves the catalytic hydrogenation of the pyrolyzed sample, followed by absorption and weighing of the water formed. In carrying out the determination it was found that the thoria-promoted catalyst used by Russell and Fulton (*5*) was the most satisfactory. A nickel-chromite catalyst was tried, but it gave incomplete hydrogenation and poor recovery of water.

It appeared to Russell and Marks (*6*) in a study of the analysis of organic compounds containing nitrogen that in the absence of oxides of carbon in the effluent gases the ter Meulen procedure could be simplified if an efficient water absorbant could be found which would not absorb ammonia. To this end reagent grade sodium hydroxide pellets were shown to have met their requirements. The authors of this paper tried several desiccants and combinations for selective absorption of water including Dehydrite, Drierite, native gypsum calcined at 250° C., plaster of Paris made into a paste and calcined at 250° C., mixtures of plaster of Paris with 1 and 5% of sodium hydroxide, pellets of potassium hydroxide, and sodium hydroxide flakes. The hydroxides of potassium and sodium were the only compounds found to be selective in that they did not absorb ammonia gas, but they also proved to be inefficient for the complete absorption of water.

The ter Meulen method suffers other handicaps which further limit its usefulness. One great disadvantage was found to be the short life of the catalyst, which limits the number of determinations that can be made with a fresh charge to about 12, and this number decreases with successive regenerations. Sulfur as reported by Dinerstein and Klipp (*3*) and by Elving and Ligett (*4*) was found to poison and hasten the deactivation of catalyst. Another disadvantage was the large and varying blank, probably due to the slow rate of reduction of the cores of the catalyst particles. Depositing the activated nickel on the surface of an inert support reduces the high blank but also shortens the life of the catalyst packing because of the small amount of material used.

Table III shows the oxygen content of samples as determined by the two procedures in question; the data presented make the distinct advantage of the Unterzaucher method readily apparent.

Table III. Comparison of Unterzaucher and ter Meulen Methods

Sample	Oxygen, %		
	Unterzaucher	ter Meulen	Theory
Benzoic acid	26.07	26.43	26.20
	26.09	26.32	
	26.09	25.99	
	26.19	25.83	
	Av. 26.11	26.14	
Nitrobenzaldehyde	31.33	37.51	31.76
	31.65		
	31.80		
	Av. 31.59		
Di-*o*-tolylguanidine	0.08	10.76	0.00
	0.06		

SUMMARY

The indirect determination of oxygen (determination by difference) is susceptible to large errors and uncertainties due to the fact that all the errors in the elemental analysis are additive. Moreover, analysis of synthetic samples for carbon and hydrogen by several laboratories, all using the Liebig method, has shown results of great variance on the same sample and of considerable divergence from theory. In the ter Meulen method it is necessary to use an absorbant that will absorb water and exclude ammonia, unless provision is made similar to that originated by ter Meulen for a combination absorbing tube for both compounds followed by a quantitative determination of the ammonia. The hydroxides of potassium and sodium in pellet form do not absorb ammonia, but neither are they efficient reagents for completely retaining water. The ter Meulen method, while proving satisfactory for some compounds, has the disadvantages inherent in a catalytic process—namely, varying catalytic activities and an acute sensitivity of the catalysts toward poisons.

The presence of inorganic oxygen compounds such as carbonates and the oxides of iron and lead will cause an error in the values for oxygen by the Unterzaucher method when oxygen is determined in organic compounds. It has been shown that sulfur-containing compounds yield hydrogen sulfide, carbon disulfide, and carbonyl sulfide when the Unterzaucher method is employed, and the latter two gases (carbon disulfide and carbonyl sulfide) are not retained by an Ascarite or potassium hydroxide scrubber. Carbon disulfide and carbonyl sulfide, if present in considerable amount, are detrimental because they have been found to liberate iodine from iodine pentoxide, thereby causing high results for oxygen. On the contrary, it is apparent that carbonyl sulfide formed during the determination has removed some of the oxygen sought, thus causing low oxygen results. For this reason the carbon disulfide and carbonyl sulfide should be retained in a liquid nitrogen trap and for a very accurate determination of oxygen the amount of carbonyl sulfide condensed should be determined and a correction applied accordingly.

The Unterzaucher method has proved more reliable than the ter Meulen method, both for uniformity of operation and for accuracy. It is also superior to the Liebig method.

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CORRECTION. In the article on "Colorimetric Microdetermination of Rhodium with 2-Mercaptobenzoxazole" [Ryan, D. E., ANAL. CHEM., **22**, 599 (1950)] on page 599, first column, under the heading "Development of Method" 240 micrograms of rhodium should have been specified, not 24, as stated.

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Specific Spot Test for Gold Employing Pararosaniline Hydrochloride

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AS A RESULT of the studies of West and Amis (*11*) of the reaction of pararosaniline hydrochloride with palladous ion, it was found that gold reacted with the reagent in such a manner as to suggest definite possibilities for use as a spot test for gold. Further investigation revealed that the reaction, the nature of which has been established by West (*9*), had a sensitivity comparable with other tests for gold described in the literature (*2–4, 7, 8*). In addition, the selectivity of the reaction was found to be far superior to most reactions involving gold, and on this basis showed special promise for spot test work.

REAGENTS

Pararosaniline hydrochloride, 0.05% aqueous solution. Ethyl acetate, C.P.

Tetrasodium pyrophosphate. Saturated solution adjusted to pH 7.0 with hydrochloric acid (prepared fresh each day).

Hydrochloric acid, C.P. (concentrated).

EXPERIMENTAL

Of the media commonly employed in spot test analysis, filter paper holds an advantage over the spot plate for use in this test because the reaction sensitivity was found to be greater using certain papers than when test tubes or spot plates were employed. The effect of using different grades of filter paper on sensitivity was found to vary to a remarkable degree, the greatest sensitivity being afforded by Schleicher and Schüll No. 595 filter paper. Diffusion of 0.05% pararosaniline hydrochloride (Schultz No. 511 from the National Aniline and Chemical Company) through this paper leaves a concentration of the reagent in the form of a ring about 7 mm. in diameter with only slight diffusion of the reagent beyond this point. Diffusion of the reagent in other papers was sometimes faster, but distribution of the reagent in those cases did not leave the ring of concentrated reagent in which the violet-black precipitate of gold fuchsin is most easily discernible when gold is to be detected in small amounts.

The order of spotting of reagent and test solution was found to be important, because gold, when spotted on paper, was apparently adsorbed so strongly that it reacted only slowly with reagent which was subsequently added to the spot. When the order of spotting was reversed, the reaction took place quickly with maximum sensitivity.

Interference studies were made according to the general procedure described by West (*10*), and palladium, rhodium, platinum, and mercurous mercury were found to react with the fuchsin in a manner analogous to gold. Attempts to eliminate these interferences were made using such complexers as ammonia, cyanide, thiocyanate, ethylenediaminetetraacetic acid, pyridine, aniline, malonate, tartrate, and citrate. In those cases where complexation of interferences was successful, gold was also masked so strongly as to prevent its reaction with pararosaniline, except that pyrophosphate was effective in sequestering palladium without adversely affecting the reactions of gold. Inasmuch as the complexation of the other interfering ions could not be effected through the use of pyrophosphate, other means were sought by which these interferences could be eliminated and specificity attained.

Lenher (*5*) reported that gold can be extracted from aqueous solutions by many organic compounds, the esters and particularly ethyl acetate being most efficient for this separation. Later Lenher and Kao (*6*) showed that maximum separation was obtained when the aqueous solutions contained hydrochloric acid in concentrations of 10% by volume. Because these extraction techniques seemed promising, an investigation was undertaken to determine the feasibility of adapting them to spot test procedures. By using a dropper pipet for extraction and phase separation, an elegant method was developed which serves to isolate gold from all potential interfering ions. [Although a medicine dropper can be used, a modified pipet (*1*) provides more thorough mixing and sharper separation of phases.] Such a procedure not only serves to prevent interferences but affords a simple, rapid method of concentrating gold from relatively dilute test solutions. In practice, the extraction involves the addition of a few drops of extractant to one or more drops of the test solution. Thorough mixing of the aqueous layer and ethyl acetate is then accomplished by drawing them into and expelling them from the dropper pipet several times, finally drawing both layers into the dropper and allowing a short time for phase separation. After the aqueous layer is disposed of, the ethyl acetate layer is added to a spot plate depression or a microbeaker where the solvent is evaporated. The auric chloride is then put into solution by means of a drop of saturated sodium pyrophosphate which serves to complex any

Table I. Scope of Interference Studies

Na^+	Be^{++}	BO_2^-	CO_3^{--}	NH_4^+	S^{--}	F^-	Fe^{++}	CN^-
Li^+	Mg^{++}	$B_4O_7^{--}$	SiO_3^{--}	NO_2^-	$S_2O_3^{--}$	Cl^-	Fe^{+++}	$Fe(CN)^{----}$
K^+	Ca^{++}	Al^{+++}	Ti^{++++}	NO_3^-	SO_3^{--}	ClO_3^-	Co^{++}	$Fe(CN)^{---}$
Cu^{++}	Zn^{++}	Sc^{+++}	GeO_3^{--}	$H_2PO_2^-$	SO_4^{--}	ClO_4^-	Co^{+++}	CNS^-
Rb^+	Sr^{++}	Ga^{+++}	Sn^{++}	HPO_3^{--}	Cr^{+++}	Mn^{++}	Ni^{++}	Acetate
Ag^+	Cd^{++}	Y^{+++}	Sn^{++++}	$P_4O_{13}^{------}$	$Cr_2O_7^{--}$	MnO_4^-	Ru^{+++}	Oxalate
Cs^+	Ba^{++}	In^{+++}	Pb^{++}	$P_6O_{18}^{------}$	CrO_4^{--}	Br^-	Rh^{+++}	Malonate
	Hg^+	La^{+++}	Zr^{++++}	PO_3^-	SeO_3^{--}	BrO_3^-	Pd^{++}	Adipate
	Hg^{++}	Ce^{+++}	Th^{++++}	HPO_4^{--}	SeO_4^{--}	I^-	Os^{+++}	Succinate
		Tl^+		$P_2O_7^{----}$	MoO_4^{--}	IO_3^-	Ir^{++++}	Phthalate
				V^{+++}	TeO_3^{--}	ReO_4^-	Pt^{++++}	Tartrate
				VO_3^-	TeO_4^{--}			Citrate
				$HAsO_3^{--}$	WO_4^{--}			Lactate
				$HAsO_4^{--}$	UO_2^{++}			Gluconate
				Sb^{+++}	UO_4^{--}			Glycol
				Sb^{+++++}				Diethylene glycol
				Bi^{+++}				Inositol
								Sorbitol
								Mannitol
								Sucrose
								Dextrose
								Aniline
								Pyridine

traces of palladium that might have been carried over because of incomplete separation.

RECOMMENDED TEST PROCEDURE

Place 1 drop to 1 ml. of test solution in a spot plate depression or microbeaker and add one tenth as much concentrated hydrochloric acid. Then add 10 to 15 drops of C.P. ethyl acetate and with a dropper pipet draw and expel the mixture six to eight times, finally drawing the contents into the pipet. Allow a few seconds for separation of the two layers and discard the aqueous layer. Wipe the tip of the pipet with filter paper and expel a small drop of the ethyl acetate solution while the tip is pressed against the paper, then transfer the remaining contents of the pipet to a second depression or microbeaker. Invariably a small drop of the aqueous layer adheres to the tip of the pipet and is released with the last drop of the ethyl acetate in the pipet. For this reason it is recommended that the final drop of ethyl acetate be retained in the pipet. By means of a piece of glass drawn into a fine tip, blow into the ethyl acetate until it has evaporated and add one drop of saturated tetrasodium pyrophosphate. Put one drop of 0.05% pararosaniline hydrochloride solution on Schleicher and Schüll No. 595 filter paper and as soon as the reagent is absorbed place the test drop in its center.

If the test drop is spotted into the reagent drop carefully it will form a convex surface with the ring of concentrated reagent as its boundary and diffusion of the test drop takes place through this ring. When gold is present in small amounts it is precipitated in the ring as a violet-black precipitate, and when present in large amounts the test color is a deep brown. The limit of identification employing this procedure is 5 micrograms of gold at a limiting concentration of 1 part in 100,000 (based on 0.5-ml. volume of test solution).

REMARKS

Interference studies were made using 1% solutions of the ions to be tested, in the presence of 0.01% gold, thus providing a ratio of interfering ion to gold of 100 to 1. The ions investigated in the interference studies are listed in Table I in their more common forms. In many instances the ions concerned are present as complexes, but where structures of such complexes may be in doubt, only the valence of the central atom is indicated.

The conditioned reaction showed no positive interferences and the only negative (masking) interferences were those given by cyanides and sulfides. The use of pyrophosphate ion to complex palladium provides a method of sequestering that ion so effectively that it is not precipitated by dimethylglyoxime and reacts with iodide only slowly to give the characteristic brown complex. Failure to eliminate the interferences of rhodium, platinum, and mercurous mercury made the use of pyrophosphate impractical for general work. In those cases in which palladium constitutes the only serious interference, pyrophosphate is an invaluable sequestrant and permits the simplification of the test by eliminating the necessity of using the extraction procedure.

Solutions of pararosaniline hydrochloride should be prepared fresh about once a month, for if allowed to stand for longer periods of time they may prove ineffective in detecting amounts of gold near the limit of identification. Freshly prepared solutions of chloroauric acid gave a much better response to the reagent than those which had been standing in the laboratory for some time.

To increase the sensitivity of the test numerous filter papers were tried, including Schleicher and Schüll Nos. 497, 589, 590, 595, 597-Y, and 604; Whatman Nos. 1, 2, 4, 5, 30, 40, 41, 42, 44, 50, and 120; Reeve-Angel Nos. 201 and 202; E&D (Chicago Apparatus Co.) Nos. 615 and 618. The paper found to be most satisfactory for this test was S. & S. No. 595, for it not only possessed excellent absorption characteristics but also was found to be of very uniform quality.

ACKNOWLEDGMENT

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Determination of Caffeine

A Rapid Semimicromethod

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BOTH the official A.O.A.C. Power-Chesnut (*2*) and the Bailey-Andrew (*1*) methods for the determination of caffeine in coffee and tea are time-consuming. Modifications (*3*) have been made in the Power-Chesnut method for commercial soluble coffees and coffee products, but the method is still lengthy. A recently reported spectrophotometric method (*6*) is more rapid and appears to give reliable results within a limited range of caffeine concentrations but is not applicable to all types of coffee. This method presents difficulties in selecting the correct clarification procedure for unknown samples when used by a routine analyst.

Taylor and Taylor (*7*) have recently published a method in which they employ lead acetate for clarification of an infusion followed by chloroform extraction in the presence of ammonium hydroxide. This method is less time-consuming than the official methods, but the ammonium hydroxide used in the method is somewhat hazardous as a nitrogen contaminant.

Hadorn and Jungkunz (*4*) report a new method whereby they extract the caffeine from an aqueous coffee extract using chloroform in the presence of ammonium hydroxide. The caffeine solution is filtered through an ammoniacal column of activated alumina. The method is open to the same objection as that of Taylor and Taylor, in that ammonium hydroxide is used and it offers little saving in time over the official methods.

A semimicromethod for the determination of caffeine in coffee and tea has been developed requiring only 15 to 25% of the time necessary for official A. O. A. C. methods, with no sacrifice in precision.

A procedure was developed for the determination of caffeine in coffee and tea, incorporating the Hengar technique (*5*) for Kjeldahl nitrogen, which offers a considerable saving in time.

EXPERIMENTAL

The accuracy of the Hengar semimicroprocedure for caffeine has been investigated. Caffeine nitrogen was quantitatively determined in authentic samples of caffeine in amounts up to 55 mg. In each case the caffeine determined agreed closely with the amount of sample taken. The results in Table I indicate that the Hengar technique is applicable to the quantitative determination of caffeine nitrogen.

Table I. Determination of Caffeine by Hengar Kjeldahl Technique

Authentic Caffeine, Mg.	Caffeine Determined by Hengar Semimicromethod, Mg.
26.8	26.5
35.4	35.3
45.7	45.6
55.8	56.3

Table II. Optimum Period for Heating Soluble Coffee with Magnesium Oxide

Heating Period, Min.	Freedom from Emulsion	Caffeine Found, %
2	Emulsion	3.28
5	Some emulsion	3.28
10	Little or no emulsion	3.23
15	No emulsion	3.25
30	No emulsion	3.26

A vacuum filtration technique for the aqueous extraction of the caffeine eliminated the time-consuming Soxhlet extraction of the Power-Chesnut method. The Bailey-Andrew method used an aliquot of the aqueous filtrate which requires uniform distribution of caffeine between the water and the magnesium oxide–ground coffee mixture. It was found that the caffeine was quantitatively extracted from a mixture of magnesium oxide and finely ground coffee by washing with hot water on a filter bed.

Clarification of the aqueous coffee extract prevents the formation of stable emulsions in the chloroform extraction. This was accomplished by heating an aqueous mixture of heavy magnesium oxide and the sample in a boiling water bath. Three grams of heavy magnesium oxide per gram of sample were necessary for satisfactory clarification after heating for a minimum of 10 minutes. There was no advantage in evaporating the samples to a dry mass as in the Power-Chesnut procedure or in boiling for 2 hours as in the Bailey-Andrew method. The results of experiments given in Table II, in which aliquot portions of a coffee solution containing 3.28% caffeine were heated with magnesium oxide, show that a heating period of 10 minutes in a boiling water bath resulted in a clarified solution which did not form an emulsion during the chloroform extraction. This technique gave reliable results.

Magnesium oxide clarifies an aqueous coffee extract by adsorption as well as by chemical reaction. Therefore it was found advantageous to pass the clarified extract through a bed of fresh magnesium oxide. In carrying out this process the samples, after heating with magnesium oxide for 10 minutes, were filtered under reduced pressure (300 to 400 mm. of mercury) through a short column of a mixture of heavy magnesium oxide and filter aid (equal parts by weight) tightly packed in a cylindrical tube (28 × 75 mm.). The column was washed with hot water to extract the caffeine. The recovery of the caffeine was over 98% in the first 75 ml. of filtrate and was quantitative in the first 125 ml. of filtrate in all cases investigated. This contrasted with the 250 ml. of filtrate collected in the slow gravity filtration of the Power-Chesnut method, which frequently allowed from 5 to 6% of the caffeine to remain in the magnesium oxide–coffee mixture.

Hot water has been used by this laboratory to extract the caffeine from the column, although cold water also gave satisfactory results.

The filtrate could be extracted directly with chloroform, but it was found that samples acidified with 5 ml. of sulfuric acid (10% by volume) presented less trouble with emulsions. A quantitative extraction of the caffeine required seven 15-ml. portions of chloroform. However, when the acidified aqueous extract was concentrated by boiling to about 50 ml., only five 15-ml. portions of chloroform were necessary. Because the capacity of the Hengar digestion flask is 100 ml., it was found convenient to limit the total chloroform extract to about 80 ml., place this directly in the Hengar flask, and then distill the chloroform using a water bath.

In the case of coffee it was found that the chloroform extract does not require an alkaline wash, but the chloroform extract from tea contains a small amount of theobromine in addition to the caffeine which is removed by washing with 2 ml. of 1% potassium hydroxide solution. Data are given in Table III to substantiate this.

The accuracy of the semimicromethod has been established by the analysis of synthetic samples of soluble decaffeinated coffee to which have been added different amounts of pure caffeine. The results are given in Table IV.

ANALYTICAL METHOD

Reagents. Magnesium oxide; heavy MgO, U.S.P. Filter aid. Sulfuric acid (10% by volume). Chloroform, U.S.P.

Procedure. Place 0.3 to 1.0 gram of the finely ground sample in a 30-ml. beaker with an amount of magnesium oxide equal to about 3 times the weight of sample and about 15 ml. of hot water. Heat in a water bath for a minimum of 10 minutes with stirring, adding hot water to maintain volume in the beaker. Transfer the sample to a tightly packed column (24 × 75 mm.) containing about 5 grams of a mixture of magnesium oxide and filter aid

Table III. Treatment of Chloroform Extract with Potassium Hydroxide

Sample	Caffeine Found in Sample, %	
	Washed with KOH	No KOH treatment
Soluble coffee	1.84	1.83
	1.82	1.83
	1.83	1.84
Tea leaves	2.86	2.92
	2.79	2.92
	2.81	2.91

Table IV. Recovery of Caffeine from a Synthetic Sample

Caffeine Calculated, Mg.	Caffeine Found, Mg.
17.40	17.40
37.90	37.40
22.20	22.10
20.95	20.96
20.95	20.75
20.95	20.80
20.95	20.80
20.95	20.80
20.95	20.80
20.95	20.75
20.95	20.80

Table V. Comparison of Results by Power-Chesnut and Semimicromethods

Sample	Caffeine, Power-Chesnut Method, % Range	Av.	Caffeine, Semimicromethod,[a] % Range	Av.
Green Santos coffee	0.99–1.07	1.03	1.01–1.07	1.05
Roasted Santos coffee	1.08–1.13	1.11	1.11–1.15	1.13
Soluble coffee product	1.65–1.66	1.66	1.65–1.72	1.68
Soluble decaffeinated coffee	0.03–0.05	0.04	0.03–0.05	0.04
Tea leaves	2.71–2.79	2.76	2.79–2.86	2.82
Soluble tea product	2.13–2.21	2.17	2.14–2.20	2.17

[a] Represents 8 determinations each sample.

Table VI. Comparison of Results by Bailey-Andrew and Semimicromethods

Sample	Caffeine, Bailey-Andrew Method, % Range	Av.	Caffeine, Semimicromethod[a], % Range	Av.
Soluble coffee	3.22–3.27	3.25	3.31–3.35	3.34
Soluble coffee product	1.74–1.80	1.77	1.81–1.82	1.82
Roasted coffee	1.13–1.15	1.14	1.23–1.24	1.23
Decaffeinated coffee	0.03–0.04	0.035	0.04–0.04	0.04

[a] Represents 3 determinations each sample.

(equal parts by weight). Wash the caffeine from the column with hot water under reduced pressure (300 to 400 mm. of mercury) and collect about 150 ml. of filtrate. Do not allow the column to become dry during the extraction process. Add 5 ml. of sulfuric acid (10% by volume) to the filtrate and reduce the volume to about 50 ml. by boiling. Cool, extract with five 15-ml. portions of chloroform, and collect the chloroform extract in a Hengar digestion flask. In the case of tea only, collect the chloroform extract in a separatory funnel and wash with 2 ml. of 1% potassium hydroxide. Transfer the chloroform to the Hengar digestion flask and wash the alkali with two 5-ml. portions of chloroform. Distill off the chloroform by heating in a water bath. Determine nitrogen by the Hengar technique for the Kjeldahl procedure.

The caffeine in coffee brew or coffee extract may be determined by using a suitable aliquot.

Time required is 2 hours for samples in duplicate.

COMPARISON OF METHODS

A variety of samples have been analyzed by the semimicromethod for comparison with the Power-Chesnut and Bailey-Andrew methods. The results in Tables V and VI show good agreement between the methods. The precision of the semimicromethod was as good as or better than any other method used in this laboratory.

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Accurate Control and Vaporizing System for Small Liquid Flows

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A system has been developed for accurately metering very small liquid flows of the order of 0.005 ml. per second, and a chamber constructed for vaporizing the liquid and mixing it with air. Any liquid may be used without individually calibrating the apparatus.

THE control and measurement of small liquid flows are an ever-occurring problem in many investigations—e.g., catalytic studies and the determination of burning velocities. In addition, it is frequently necessary to transform the liquid into the vapor state without interrupting the steady flow. An apparatus has been constructed which fulfills these needs with the added advantage that the rate of liquid feed is independent of the material used. It is thus only necessary to calibrate the system once. Even lower flows than those used in this work, 0.005 to 0.05 ml. per second, are readily possible with the arrangement.

Hogg, Verheus, and Zuiderweg (*2*) suggested a system in which the liquid was forced out of a feed tube by a mercury column, the mercury being raised by a synchronous motor and pulley arrangement. Although this gives very constant flows if proper precautions are taken to prevent slippage in the pulley system, the flow rate can be varied only by changing the gear ratio connecting the motor to the pulley or by changing the size of the pulley wheel. The application of sonic orifice flowmeters (*1*) to the problem permits the mercury column to be raised at a linear rate which is continuously variable by changing the pressure on the sonic orifice. The sonic orifice system is also superior to the synchronous motor and pulley arrangement in that it conveniently permits operation for longer periods of time. This is possible because the feed tube can be made longer without complicating the mechanical system as would be necessary with a pulley arrangement—it is only necessary to increase the pressure on the upstream side of the orifice.

LIQUID FEED SYSTEM

The liquid feed system is shown in Figure 1. An increase in pressure in the air chamber causes the mercury in the liquid feed tube to rise, forcing the liquid into the mixing chamber. Because the flow through a sonic orifice flowmeter is independent of the downstream pressure (*1*) and linearly dependent on the upstream pressure, the increase in pressure in the air chamber, and thus the liquid feed rate, is determined by the setting of the upstream pressure. The rate of flow through a sonic orifice is given by Equation 1:

$$V = CAP\sqrt{\frac{K}{\rho}} \qquad (1)$$

where V = volumetric flow rate, C = discharge coefficient, A =

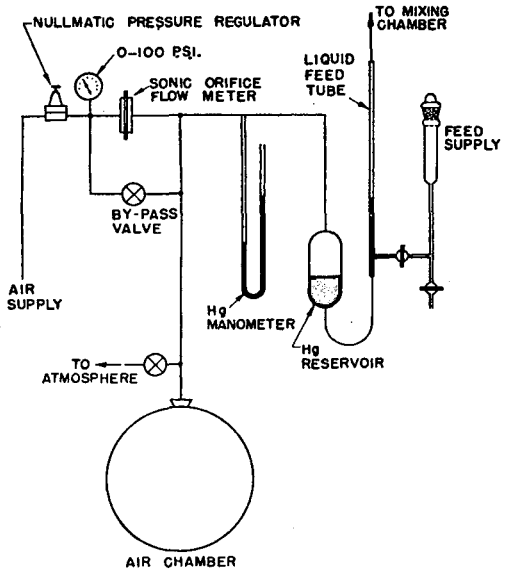

Figure 1. Liquid Flow Control System

orifice cross-sectional area, P = upstream pressure, ρ = gas density, and K = a function of γ ($\gamma = C_p/C_v$).

An expression for the volumetric rate of liquid flow can be readily derived by equating the pressure in the mercury reservoir at any given instant of time to the pressure in the liquid feed tube —that is, the pressure in the air chamber plus the hydrostatic pressure of the mercury in the mercury reservoir is balanced by the sum of the hydrostatic pressure of the mercury in the liquid feed tube, the hydrostatic pressure of the liquid, the pressure drop due to the flowing liquid, and the static pressure in the mixing chamber. Substituting in the expressions for pressure, and differentiating with respect to time, one obtains the formula:

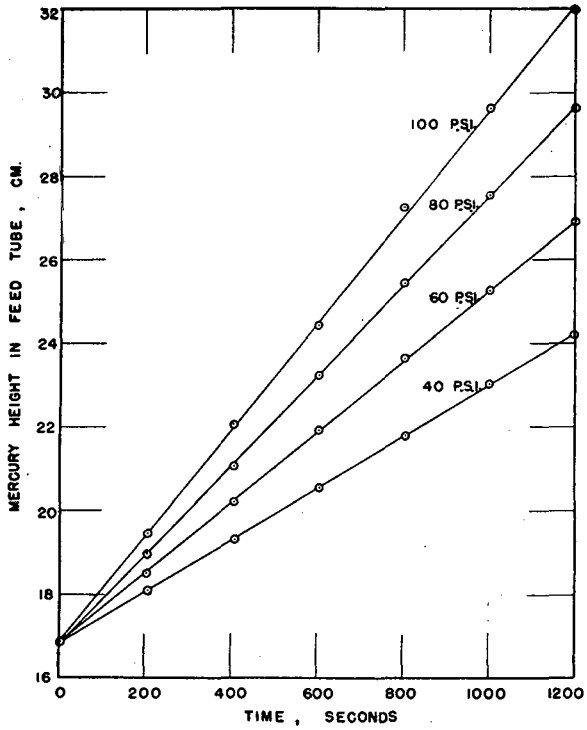

Figure 2. Calibration of Liquid Feed System for 0.06-Mm. Jewel

$$V_{liq.} = \frac{\pi P_1}{4gV_a}\left[\frac{\rho_{Hg} - \rho_{liq.}}{d^2} + \frac{\rho_{Hg}}{D^2}\right]^{-1} \times V \quad (2)$$

where g = acceleration of gravity, d = diameter of liquid feed tube, D = diameter of mercury reservoir, ρ_{Hg} = density of mercury, $\rho_{liq.}$ = density of liquid, P_1 = pressure at which V is measured (atmospheric), and V_a = volume of air chamber and associated leads. In differentiating the equation for pressure, it is assumed that the mixing chamber pressure does not change with time.

Because differentiation with respect to time of the equation for flow through a constriction gives zero, the pressure drop due to the flowing liquid has no effect on the rate of flow. The calibration is, therefore, independent of liquid viscosity. Any pressure drop through a small constriction will, of course, have to be balanced by the total pressure on the left of the mercury reservoir (Figure 1). Although usual laboratory temperature variations, or the rate of such changes, are insufficient to cause errors, it may be necessary for extremely accurate measurements to insulate the air chamber thermally. Variations in liquid density will, in general, make only a small change in flow rate (Equation 2), because the density of mercury is roughly fifteen times the density of most organic liquids and these densities vary over a relatively narrow range. When the density of the material is sufficiently different from the calibrating liquid, a correction can be easily made by applying Equation 2. To determine the weight of liquid or the number of moles delivered per unit time, it is only necessary to know the liquid density.

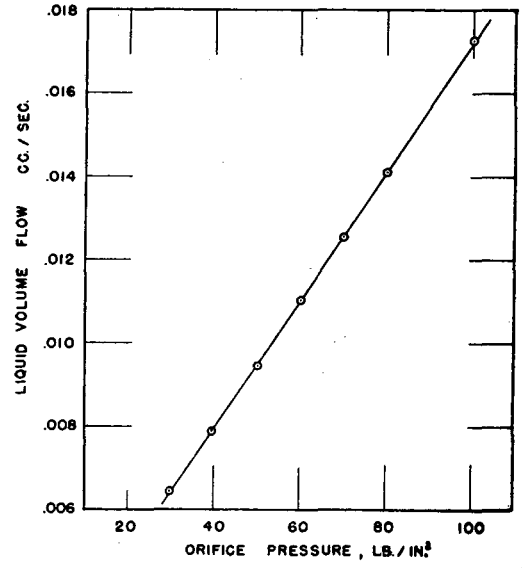

Figure 3. Calibration Curve for 0.06-Mm. Jewel

In the particular experimental setup that has been used, the sonic orifice jewel (synthetic ruby bearing jewel) diameters varied from 0.06 to 0.12 mm., the volume of the air chamber was roughly 35 liters, the diameter of the mercury reservoir was 2.8 cm., and the liquid feed tube was 60 cm. long and had a diameter of 1.270 cm. (Ace Trubore round Pyrex tube). Liquid flow rates in the range of 0.005 to 0.05 ml. per second have been used. This range can be easily extended with orifices of different sizes. The method is capable of producing even lower flow rates by increasing the air chamber volume, V_a, or by decreasing the diameter of the fuel feed tube, d, or the mercury reservoir, D.

In practice the system is calibrated by determining the change in mercury height in the feed tube as a function of time for various pressures upstream from the sonic orifice. This gives a straight line (Figure 2), the slope of which, in combination with the feed tube diameter, yields the volumetric rate of feed. A plot of the

volumetric rate of liquid feed against the orifice pressure also gives a straight line, as it should (Figure 3). When only a small quantity of sample is available, or it is desired to operate for a short length of time, the by-pass valve is opened and the mercury height in the feed tube raised until the liquid enters the mixing chamber. At the end of a run, the valve to the atmosphere is opened, releasing the pressure in the system so that liquid from the "feed supply" reservoir may be fed into the "liquid feed tube," preparatory for the next run.

VAPORIZATION AND MIXING

If it is necessary to vaporize the liquid steadily and mix it with a gas, this can be accomplished with the mixing chamber shown in Figure 4.

The glass nozzle extends just a fraction above the $^3/_{64}$-inch hole, so that no aspirator action is obtained which would give oscillations if present. The rapid passage of air over the liquid droplets, formed at the tip of the nozzle, gives a very fine spray. The chamber and associated tubing are all stainless steel except for the glass tube from the liquid control system; thus any liquid can be used which does not attack glass or stainless steel. Because the tube enters the chamber at a position where only air is present in the writer's setup, the glass-metal seal is made with de Khotinsky cement. In a later setup hypodermic stainless steel tubing was substituted for the glass nozzle. By means of the control valve on the gas inlet side, a pressure of approximately 10 to 15 pounds per square inch gage is maintained across the small annular air opening around the nozzle; some of the air is by-passed into the top of the chamber by the control valve. The heat of vaporization is furnished by heating the mixing chamber and the by-pass inlet gas line with an electric furnace.

Of the several types of mixing and vaporization methods tried at these very small flow rates, this is the only one which has performed satisfactorily under routine operation without oscillations.

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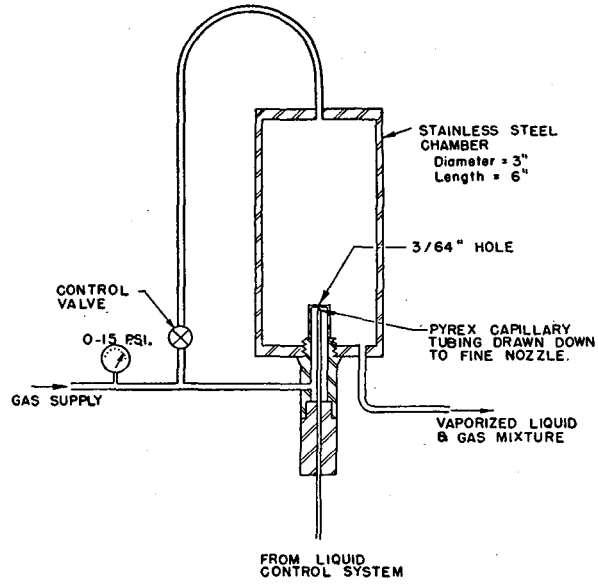

Figure 4. Vaporization and Mixing Chamber

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RECEIVED December 10, 1949.

NOTES ON ANALYTICAL PROCEDURES . . .

Precipitation of Oxalates from Homogeneous Solution

Separation and Volumetric Estimation of Zinc

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IN an earlier paper (*2*) it was shown that magnesium could be precipitated in an easily filtrable form from 85% acetic acid solution by the slow decomposition of ethyl oxalate, thus avoiding the experimental difficulties formerly encountered in the separation of magnesium oxalate for the indirect determination of magnesium with permanganate. This paper summarizes the results of experiments on the precipitation of zinc by this same technique. With slight modification, the procedure for the precipitation of magnesium is also suitable for zinc. If used without modification, the zinc oxalate is precipitated in very large crystals that are not only inconvenient to filter but apparently impure. Such crystals are formed when the precipitation from homogeneous solution occurs at too slow a rate. By using more ethyl oxalate initially the rate is increased, crystals of desirable physical properties and purity are obtained, and the time of precipitation is shortened.

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PROCEDURE

Concentrate the neutral zinc solution in a 250-ml. beaker to a volume of 10 to 12 ml. or dissolve the residue of dried salts containing the zinc in 11 ml. of water. Add 85 ml. of glacial acetic acid in which 1 gram of ammonium acetate has been dissolved. Then add 4 ml. of ethyl oxalate, stir well, and heat rapidly to approximately 100° C. Cover the beaker with a watch glass and place on a hot plate so regulated that the solution is maintained at approximately this same temperature. Allow 1.5 hours for precipitation. If there is any doubt as to maintenance of the recommended temperature during this period, add, 5 minutes before filtration, 5 ml. of 85% acetic acid that has been saturated with ammonium oxalate at room temperature. Filter and wash

Table I. Determinations of Zinc by Recommended Procedure

Zn Taken	Zn Found	Difference, Error
Gram	*Gram*	*Gram*
0.0010	0.0009	−0.0001
	0.0010	0.0000
	0.0010	0.0000
0.0049	0.0049	0.0000
	0.0049	0.0000
	0.0051	+0.0002
0.0100	0.0100	0.0000
	0.0102	+0.0002
	0.0102	+0.0002
0.0500	0.0499	−0.0001
	0.0501	+0.0001
	0.0503	+0.0003

Table II. Precipitation in 70% Acetic Acid Solution

Anion Present	Zn Taken	Zn Found	Difference, Error
	Gram	*Gram*	*Gram*
Chloride	0.0010	0.0002	−0.0008
		0.0003	−0.0007
		0.0003	−0.0007
Sulfate	0.0010	0.0006	−0.0004
		0.0007	−0.0003
		0.0007	−0.0003
Chloride	0.0049	0.0050	+0.0001
		0.0050	+0.0001
Sulfate	0.0100	0.0101	+0.0001
		0.0102	+0.0002
Chloride	0.0250	0.0248	−0.0002
		0.0251	+0.0001
Sulfate	0.0250	0.0250	0.0000
		0.0251	+0.0001

the precipitate, dissolve it, and titrate the solution as in the procedure for magnesium.

This procedure is suitable for about 0.5 to 50 mg. of zinc. Larger amounts require a longer time for precipitation and the results may not be satisfactory.

Care should be taken not to use acetic acid that has been in contact with paraffin on closures of bottles, as the paraffin may separate when the acid is added to the aqueous zinc solution. The use of partly hydrolyzed ethyl oxalate must be avoided (*2*).

TEST DETERMINATIONS

For these determinations, and for certain other experiments described below, standard zinc solutions were prepared by dissolving accurately weighed amounts of highly pure zinc in a slight excess of hydrochloric acid, and diluting to volume in calibrated flasks. Suitable aliquot portions were taken and evaporated to dryness to remove free acid, and the zinc content was determined by the above procedure. As shown in Table I, satisfactory results were obtained.

VARIOUS EXPERIMENTS

Because Elving and Lamkin (*1*) state that "zinc can be completely precipitated as oxalate in 70% acetic acid medium," the question arose as to whether the use of a medium as concentrated as 85% was really necessary. A series of test determinations was run in which the zinc was precipitated homogeneously as oxalate from 70% acetic acid solution, by the method given above, except for the concentration of acetic acid (Table II). As Elving and Lamkin ran their test determinations with sulfate solutions, the test determinations were made on sulfate as well as chloride solutions.

With the smallest quantity of zinc all the results are low, and when the zinc is in the form of sulfate they check closely with the corresponding results given by Elving and Lamkin (*1*, Table II). This is important, as showing that the low results on small quantities of zinc cannot be ascribed to the difference in the two methods of precipitation. It is likely that these low results are caused by insufficient insolubility of the precipitate in 70% acetic acid. The fact that satisfactory results are obtained with larger quantities of zinc by both methods may be due to retention of extra oxalate by the precipitate, so that possibly the results in 70% solution are satisfactory only because of a compensating effect. The need for having the concentration of acetic acid as high as 85% in order to obtain satisfactory results in the precipitation and determination of small quantities of zinc is further shown by Table III. In these determinations the zinc was initially present as chloride.

Table II indicates that when zinc is initially present as sulfate in precipitations made in 70% acetic acid, the results tend to be higher than when present as chloride, especially with a small amount of zinc. This same effect was found for precipitations made in 85% acid, except that the effect was greater (Table IV).

These high results are apparently caused by the retention of extra oxalate by the precipitate. On the other hand, low results may be obtained when an attempt is made to determine much larger amounts of zinc—i.e., 100 mg. or more—in the form of sulfate, because the amount of zinc sulfate present considerably exceeds the solubility of this salt in the total volume of solution. In general, therefore, sulfate interferes with the determination of zinc when precipitated as oxalate in 85% acetic acid solution. In 70% acetic acid, according to Elving and Lamkin and the experiments of the present investigation, satisfactory results may be obtained when sulfate is present, but only for a limited range in the amount of zinc.

Because of this interference from sulfate, and because sulfate is often present in solutions in which zinc is to be determined, the possibility of removing or destroying the sulfate before applying this procedure for zinc was tested. Removal with barium ion or lead ion is unsuitable, because any excess of these precipitating ions interferes in the precipitation of zinc oxalate. Though removal of the excess is possible if lead is used, this is objectionable as involving still another step. Actual destruction of the sulfate appears to be better than its removal by precipitation. By treating zinc sulfate residues with a sufficient excess of pure concentrated hydriodic acid and evaporating to dryness, sulfate is completely destroyed and the zinc is quantitatively converted to the iodide. The easily available commercial acid containing hypophosphorous acid as a preservative unfortunately cannot be used for this purpose, because the residue after evaporation then contains zinc salts of acids of phosphorus that are insoluble in water

Table III. Effect of Concentration of Acetic Acid on Results Obtained with a Small Quantity of Zinc

Acetic acid concentration, %	70	75	80	85
Zn taken, gram	0.0019	0.0019	0.0019	0.0019
Zn found, gram	0.0015	0.0015	0.0016	0.0018
	0.0016	0.0015	0.0017	0.0018
	0.0017	0.0016	0.0017	0.0018
	0.0017	0.0017	0.0017	0.0018
	0.0018	0.0018	0.0018	0.0020
	0.0018	0.0019	0.0021	0.0020
Av. Zn found, gram	0.0017	0.0017	0.0018	0.0019
Av. difference error, gram	−0.0002	−0.0002	−0.0001	0.0000

Table IV. High Results in 85% Acetic Acid Solution Caused by Sulfate

Anion Present	Zn Taken	Zn Found	Difference, Error
	Gram	*Gram*	*Gram*
Chloride	0.0019	0.0018	−0.0001
		0.0020	+0.0001
Sulfate	0.0019	0.0024	+0.0005
		0.0029	+0.0010
Chloride	0.0100	0.0100	0.0000
		0.0102	+0.0002
Sulfate	0.0100	0.0104	+0.0004
		0.0105	+0.0005

and in acetic acid solutions. For the experiments the pure acid was made by the interaction of iodine and hydrogen sulfide. It was found that 8 ml. of the constant boiling acid for each 100 mg. of zinc sulfate were sufficient for the complete destruction of the sulfate on a single evaporation. The results of determinations on zinc iodide residues obtained by such treatment were, however, not so good as those on chloride solutions; they generally were a little high, in part at least because of slight retention of iodide in the precipitate of zinc oxalate. Because of the general unavailability of pure hydriodic acid commercially, this means of destroying sulfate is of no great practical value in this procedure for zinc. It is, however, of interest as a widely applicable general method for destroying sulfate, and it may prove useful in other procedures involving nonaqueous solvents, where the presence of sulfates is undesirable because of their general low solubility in such solvents.

Elving and Lamkin (*1*) found that 10 mg. of ferric iron in 10 ml. of 70% acetic acid gave no precipitate with oxalate, and that by their procedure satisfactory results were obtained for the zinc content of alloys that contained low percentages of iron. They give no information on the behavior of larger quantities of iron, nor do they appear to have made systematic experiments on the determination of zinc in the presence of various amounts of iron. When the present procedure is used, as much as 10 mg. of either ferrous or ferric iron as chloride may be present alone without giving any precipitate, but when zinc is also present, as is shown by Table V, even 5 mg. will cause high results for zinc by reason of coprecipitation of the iron as oxalate. The occurrence of coprecipitation was deduced not only from these quantitative results but from the visible discoloration of the precipitates of zinc oxalate obtained in the experiments. The results in Table V also show that the error from coprecipitation increases with increase in quantity of either zinc or iron and that ferrous iron interferes more than ferric. This interference from iron may obviously cause large errors in the determination of zinc by this procedure, and therefore all except minute amounts of iron must be removed beforehand.

Table V. Interference from Iron in 85% Acetic Acid Solution

Oxidation State of Added Fe	Fe Present	Zn Taken	Apparent Amount of Zn Found	Difference, Error
	Gram	*Gram*	*Gram*	*Gram*
II	0.0101	0.0000	0.0000	0.0000
	0.0101	0.0019	0.0027	+0.0008
	0.0101	0.0500	0.0529	+0.0029
II	0.0052	0.0100	0.0106	+0.0006
	0.0100	0.0100	0.0114	+0.0014
	0.0528	0.0100	0.0397	+0.0297
III	0.0098	0.0000	0.0002	+0.0002
	0.0098	0.0019	0.0022	+0.0003
	0.0098	0.0500	0.0515	+0.0015
III	0.0051	0.0100	0.0107	+0.0007
	0.0098	0.0100	0.0111	+0.0011
	0.0500	0.0100	0.0114	+0.0014

LIMITATION OF APPLICATION

The practical application of this procedure is limited because of interference from various ions, some of them commonly associated with zinc. Sulfate interferes to some extent and iron interferes seriously. Cadmium, copper, lead, calcium, and magnesium, and any other metals that precipitate as oxalates in 85% acetic acid solution, must be absent. In practice this procedure appears to be most useful for the accurate volumetric determination of zinc in certain mixtures or preparations in which zinc is the only metal present, and in solutions that contain no interfering ions or from which interfering ions may be readily removed.

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Photometric Determination of Available Phosphorus Pentoxide in Fertilizers

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ACCORDING to the method of the Association of Official Agricultural Chemists (*1*), the available phosphorus pentoxide in acidulated samples, dicalcium phosphate, precipitated bone phosphate, and precipitated bone is obtained by subtracting the citrate-insoluble phosphorus pentoxide from the total phosphorus pentoxide. Thus, two analyses are necessary to obtain a single result. Obviously, a more direct method would provide a saving in time and a reduction of the possibility of error. The method proposed in 1938 by MacIntire, Shaw, and Hardin (*6*) was based on a steam digestion but, though promising, has apparently not found general acceptance.

In the official method (*1*) for determining citrate-insoluble phosphorus pentoxide the sample is washed with water and then digested with neutral ammonium citrate, and phosphorus pentoxide is determined in the residue. Analysis of the combined water washings and filtrate from the citrate digestion would give the available phosphorus pentoxide directly, but this cannot be done by the volumetric molybdate method because citrate interferes with precipitation of the phosphorus as the phosphomolybdate. Recentely Barton (*2*) has shown that the photometric phosphovanadomolybdate method is suitable for analysis of phosphate rock. Kitson and Mellon (*4*) in a thorough study have shown that the ions likely to be present in the analysis of fertilizer would not cause interference. Others (*5*, *7*, *8*) have demonstrated the application of the method for analysis of phosphorus in a variety of materials. This study was undertaken to determine whether the same method could be adapted to analysis of combined water washings and citrate filtrate.

REAGENTS

Prepare vanadomolybdate according to the directions of Barton for the mixed reagent. Dissolve 40 grams of "acid molybdic 85%" in 400 ml. of water, dissolve 1.0 gram of ammonium vanadate in 300 ml. of water, and add 200 ml. of concentrated nitric acid. Allow the two solutions to cool and mix by pouring the molybdate solution into the vanadate solution. Dilute to 1 liter.

Prepare neutral ammonium citrate according to directions of the Association of Official Agricultural Chemists (*1*). Dissolve 370 grams of crystallized citric acid in 1500 ml. of water and nearly neutralize by adding 345 ml. of ammonium hydroxide (28 to 29% NH_3). Carefully adjust to pH 7 and dilute if necessary to a specific gravity of 1.09 to 20° C.

Prepare standard phosphorus pentoxide solution by dissolving 0.4792 gram of potassium dihydrogen phosphate in 1 liter of

water. This solution contains 0.25 mg. of phosphorus pentoxide per ml.

Nitric acid, C.P., concentrated.

PROCEDURE

Place a 1-gram sample on a 9-cm. filter paper and wash ten times with 10-ml. portions of distilled water. Save the washings and add 25 ml. of concentrated nitric acid to prevent reversion and to reduce cloudiness when the citrate filtrate is added. Transfer the filter and residue, within 1 hour, to a 250-ml. flask containing 100 ml. of the ammonium citrate solution previously heated to 65° C. in a water bath. Close the flask tightly and shake vigorously until the paper is reduced to a pulp, relieving the pressure by momentarily removing the stopper. Loosely stopper the flask to prevent evaporation and return it to the bath. Maintain contents of flask at exactly 65° C., keeping the level of water in the bath above that of the solution in the flask. Shake the flask every 5 minutes. Digest for exactly 1 hour. At the end of the digestion period filter with suction into the water washings and wash with water at 65° C. until a volume of nearly 500 ml. is reached. Let cool, adjust the volume to exactly 500 ml., and transfer a 5-ml. aliquot to a 100-ml. volumetric flask. Add 25 ml. of water and 25 ml. of the vanadomolybdate reagent, make up to the mark, mix thoroughly, and let stand 10 minutes for development of color.

Determine the optical density at 400 mμ using a Beckman Model DU spectrophotometer with a 1-cm. cell. A Fisher electrophotometer or other similar instrument may be used for measurement of transmittance. Because of the color of the reagent, it is necessary to place a reagent blank in the reference cell. Barton has shown that the color is temperature-sensitive, so standard solutions must be run with each determination. Select aliquots of the standard phosphorus solution corresponding to the range of concentration of phosphorus expected, add 25 ml. of nitric acid and 100 ml. of ammonium citrate solution, dilute to 500 ml., develop color as directed, and measure the optical density as directed above. Prepare a standard curve by plotting the values so obtained.

DATA AND DISCUSSION

The method was applied to analysis of a number of fertilizers in a routine manner; no special precautions were taken to ensure greater accuracy than would be expected from a chemist who must make several thousand such determinations per year. In Table I analyses by the colorimetric method and by the A.O.A.C. method in this laboratory are compared with the average results of analysis on several Magruder check samples. These samples are prepared and sent out by the Royster Guano Company each month and are analyzed by eighty or more state and commercial chemists using the A.O.A.C. methods.

Table I. Analysis of Magruder Check Samples

		% Available P_2O_5		
	Sample	Average analysis	A.O.A.C. method, this lab.	Colorimetric method
June 1948	3-9-6	9.2	9.5	9.2
July 1948	Superphosphate	20.4	21.1	20.5
August 1948	3-12-6	12.5	12.3	12.5
September 1948	6-8-6	8.2	8.2	7.8
October 1948	0-8-30	8.6	8.9	8.6
November 1948	5-10-5	10.8	11.1	10.8

Table II. Analysis of Commercial Fertilizers

		% Available P_2O_5	
Lab. No.	Sample	A.O.A.C. Method	Colorimetric method
6	Ammonium phosphate sulfate	21.3	20.5
8	5-10-5	9.8	9.8
25	6-10-4	9.7	9.5
33	Superphosphate	21.0	20.4
97	8-8-8	7.9	8.1
334	Ammonium phosphate sulfate	20.3	19.9
335	Ammonium phosphate sulfate	20.4	19.9
338	5-10-5	9.7	9.8
339	5-10-5	10.0	9.8
341	5-10-5	9.6	9.3
374	Superphosphate	18.6	18.5

Table II gives a comparison of the colorimetric method with routine analyses of official fertilizer samples submitted by the Louisiana Department of Agriculture.

The water-soluble phosphoric acid in a fertilizer plus that dissolved by neutral ammonium citrate under conditions specified by the official method gives a measure of the amount of phosphoric acid available to plants. In the official method this value is obtained by subtracting the amount of citrate-insoluble phosphoric acid from the total phosphoric acid. In the photometric method the amount of soluble phosphoric acid is determined directly on the combined filtrates which are obtained in the official method for citrate-insoluble phosphoric acid. The only deviation from the official procedure is the use of less water for washing the sample before citrate digestion. This is done to keep the volume within convenient limits, and according to the work of Jacob and Tremearne (*3*) should cause little error in analyzing the types of samples commonly submitted to fertilizer chemists. The photometric method should give results comparable with the official method.

Tables I and II show that good agreement is obtained between the two methods. From Table III it may be seen that the photometric method gives results that are reproducible within the limits expected in ordinary fertilizer analysis.

Table III. Reproducibility of Analysis by Photometric Method

	% Available P_2O_5		
Sample	I	II	III
6-10-4	10.3	10.3	10.1
10-20-10	18.0	18.1	18.2
4-12-4	10.7	10.8	10.8
3-12-12	11.1	11.2	11.3
Superphosphate	19.2	19.1	19.1

The official method, though susceptible of a high degree of accuracy, is subject to error due to time and temperature of digestion, method of precipitation, washing of precipitate, etc. Examination of the monthly reports of analysis of the Magruder check samples customarily shows a maximum variation of ±0.5% from the average value. It is believed that the photometric method is well within this range of accuracy for routine determination of available phosphoric acid in commercial fertilizers.

The chief advantage of this method is the elimination of a large number of laboratory operations, such as weighing, solution of samples, precipitation, filtration, washing of precipitates, and titration, many of which are time-consuming. There is also a considerable saving in cost of reagents.

SUMMARY AND CONCLUSIONS

A study of the application of the photometric vanadomolybdate method for determination of available phosphoric acid in fertilizers has shown the method to be sufficiently accurate for routine purposes. Analysis can be completed in approximately half the time required for the official A.O.A.C. method. The method should prove particularly useful to fertilizer plant chemists.

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Medium-Sized Laboratory Apparatus for Distribution Analysis of Mixtures

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IN 1932 Jantzen (*5*), working at the University of Hamburg on coal tar bases, gave a brief description of a multiple U-tube extraction apparatus which was employed at times in preliminary work. For difficult separations he seems to have obtained better results with spinning rod extraction columns which were developed alongside (*6*), and reported results obtained with these.

Between 1938 and 1942 a number of spinning rod columns were used at the University of Texas in the separation of petroleum acids. Especially when used with reflux they were found very valuable for acids with less than ten carbon atoms, but the higher acids showed such a strong tendency to emulsify that very dilute solutions had to be employed. This, together with the fact that very reliable proportioning pumps have to be used, made it appear best to try to avoid the use of these columns when a research project dealing with petroleum acids with twelve or more carbon atoms was started.

In view of the marked success achieved by Craig and coworkers (*1, 3, 4*) with their distribution apparatus, the multiple U-tube scheme of Jantzen was reconsidered and a 20-tube apparatus was constructed and tested. The principle involved is entirely similar to that of the Craig apparatus.

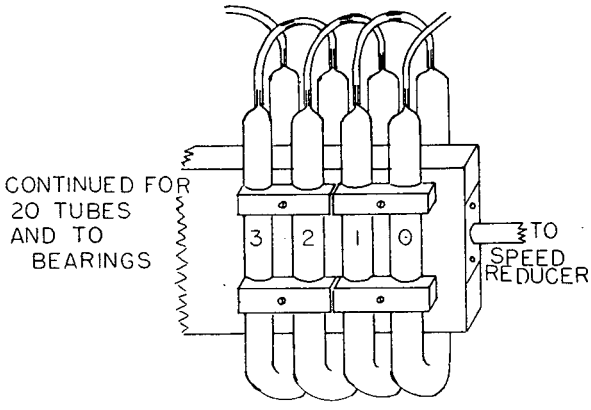

Figure 1. Arrangement of Tubes in Rotating Member

A four-tube portion of the distributing section is shown in Figure 1. The borosilicate glass U-tubes have a capacity of 125 ml. and this volume should be the same for all U-tubes used. Tips 4 mm. in outside diameter and 1.5 cm. long are sealed onto each tube, and Tygon tubing containing a short section of 1-mm. capillary tubing is used to connect the U-tubes as shown. Liquids are introduced and removed from the apparatus through similar tubing with pinchclamps or glass plugs on tubes 1 and 20. Slight air pressure or an elevated reservoir is required to force the liquids from tube to tube.

OPERATION

In this apparatus it is possible to move either the light or the heavy phase and leave the other in fixed tubes, or to disconnect the tenth tube, add the mixture to it, and move both heavy and light phases after each rotation period.

If we assume that a mixture of similar compounds is dissolved in water (heavy phase) and that this layer is to come in contact with benzene as the light and moving phase, the procedure is as follows:

The apparatus is completely filled with water (previously saturated with benzene). It is then set so that the tubes are in position 1, light phase moving (Figure 2), and the benzene is permitted to enter from the reservoir. As benzene enters, the tubes are slowly rotated counterclockwise through position 2, finally to position 3. The flow of benzene is stopped just as the tube is half-filled, as shown in position 3. The benzene layer previously in this tube has, of course, been forced into tube 1 (if, according to Craig's convention, we designate the first tube as tube 0), and a similar transfer has occurred in all subsequent tubes that were in operation. If the heavy phase had been the moving one, the corresponding positions of the tubes would have been those shown for heavy phase moving.

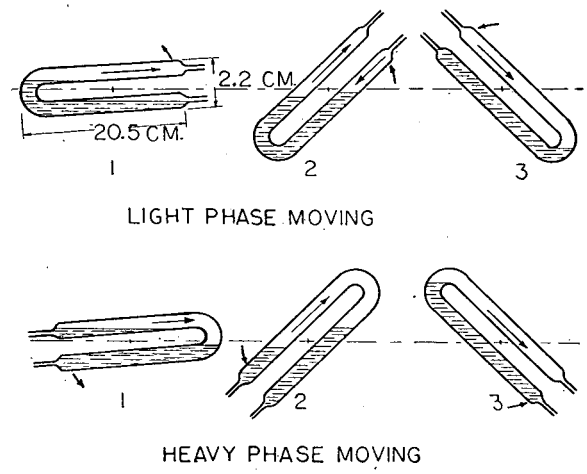

Figure 2. Positions of Tubes during Transfer of Phases

The sequence of operations is continued until the first benzene layer is in tube 20 or, in case the mixture moves slowly, the operations can be continued until the first component has just arrived in tube 20 or passed through tube 20. As in the case of the Craig machine, operations may be varied in a number of ways.

Although the Craig apparatus permits the sequence of operations to be completed more rapidly, the U-tube apparatus is leakproof, can be constructed at slight cost, and, in organic chemis-

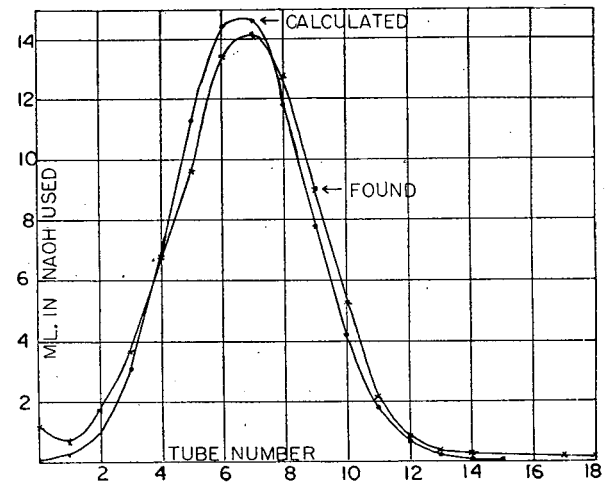

Figure 3. Distribution of Benzoic Acid

try, has the great advantage that it can process much larger quantities of material than the Craig apparatus.

Although the principle involved is identical with that used in Craig's machine, data on the distribution of benzoic acid were obtained and results compared with the calculated values (Figure 3). Craig's system of equal volumes of methanol and water as heavy phase and equal volumes of Skellysolve C and benzene as the light phase was used (*2*). The distribution constant for the system used by the authors was found to be 0.55 instead of his value, presumably because of difference in composition of the hydrocarbon mixture. The agreement between calculated and determined values is satisfactory, showing that errors due to slight difference in volumes of the U-tubes and to inaccurate cutting at position 3 are not serious. The results show strikingly, however, the effect of presence of a small amount of low molecular weight acid in tubes 0 to 2 and of failure to permit emulsions to settle completely before proceeding to the next stage (tubes 12 to 18).

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Molecular Still

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SOME improvements in the vertical-type molecular still have been made during the past few years (*1–6*). The present note describes a cyclic still, essentially following the design of Quackenbush and Steenbock (*6*), using a magnetically driven metallic rotor.

Because some difficulties had been encountered with the glass rotor suggested by Quackenbush and Steenbock (*6*), it seemed advisable to elaborate on their basic design. A photograph of the molecular still, ready for operation but without the protective Lucite shield, is shown in Figure 1.

The liquid to be distilled can be introduced into the still through stopcock *St* and allowed to drain into storage chamber *H*. The magnetic pump, *P*, lifts the liquid upward into chamber *F*, which

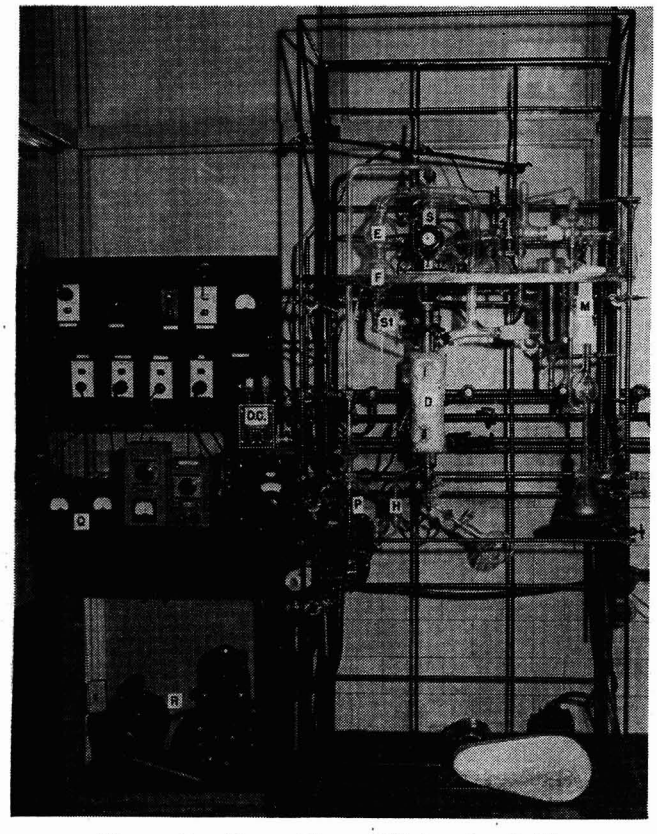

Figure 1. Front View of Molecular Still

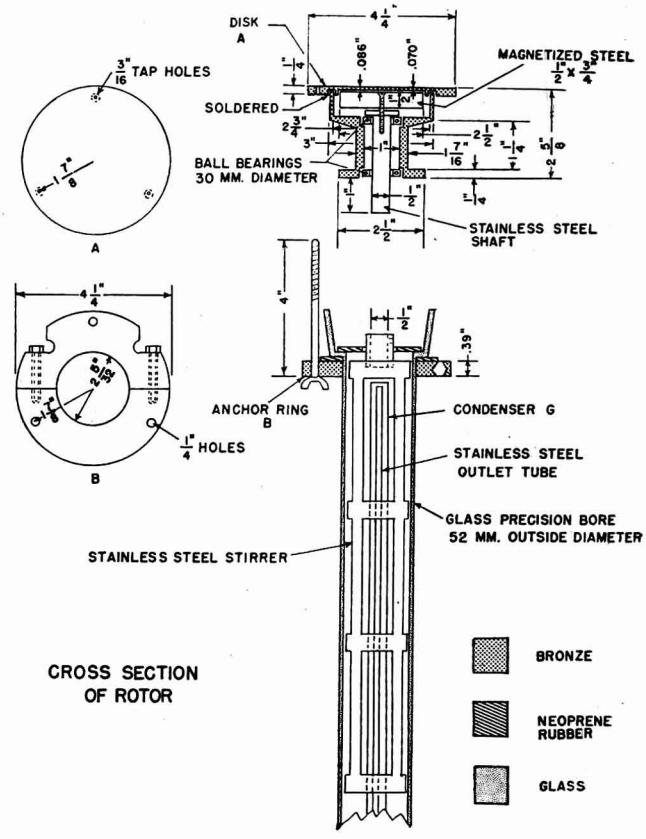

Figure 2

provides for partial degassing. This pump is made from a hollowed iron core containing one glass ball check valve, with another check valve about 3 inches above in the system. The iron core piston is supported on a Nichrome wire coil spring, and is normally outside the field of the surrounding coil. The coil is a 110-volt alternating current, No. 40C11560 (Phillips Control Corporation) unit, which sucks the piston downward upon being actuated. Making and breaking of contact to this coil is provided by a microswitch, which in turn is actuated by the ex-center wheel of a geared-down motor. This motor is furthermore controlled by a Varitran autotransformer, and thus pumping speeds to correspond to a 1-second cycle (about 1 ml. per second) can be realized.

A second chamber, *E*, immediately above *F* avoids spattering of the liquid material in the system. From *F*, the distilland flows through stopcock *St*, which serves to regulate the flow rate, into

distillation chamber D, which contains the stainless steel rotor, comprising clutch magnet, shaft, ball bearings, and stirrer, the construction of which is shown in detail in Figure 2.

The rotor consists of a brass housing supported on top of the distilling chamber on ball bearings, and a stainless steel stirrer attached to it. The precision-built stirrer is aligned perpendicularly to the distilling chamber with a level and is centered by proper clamping of the anchor ring, B, to the disk, A, of the metal housing. An Alnico magnet, connected to a high-torque direct current motor (G. K. Heller Company), is centered and supported very close to the surface of A. The cylindrical stirrer has twelve equal sections cut out for reducing weight and allowing distillation to take place. The precision glass tubing (Glo-Tech precision-bore borosilicate glass tubing, obtained from Fischer & Porter Co., Hatboro, Pa., and flanged on a glass-working lathe), which serves as the wall of the distillation chamber, D, is heated from the outside by a Glas-Col mantle, the temperature of which is controlled by another Varitran and is measured by a Brown potentiometer. The clearance between the stirrer and the inner wall of the precision-bore tube is 0.005 inch.

The condenser, G, is equipped with both inlet and outlet stainless steel tubing for liquid cooling.

The system is evacuated by a Cenco Hypervac backing pump, R, and a two-stage oil diffusion pump, S, manufactured by Distillation Products, Inc. Vacuum control is maintained by the Pirani gage, Q, and the McLeod gage, M.

The amount to be distilled is governed by the dimensions of storage chamber H and charges from 100 ml. to 1 liter can be recycled conveniently.

The unit has been used successfully in the distillation of certain natural products which proved refractory to conventional distillation techniques. The results of this work will be reported elsewhere.

ACKNOWLEDGMENT

The assistance of H. Rayford Fry, Jr., and Frederick J. Schultz of the mechanical department of Winthrop-Stearns, Inc., is gratefully acknowledged. Thanks are also due to G. W. Ewing, Union College, Schenectady, N. Y., for help in the original design of the unit.

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RECEIVED October 28, 1949.

Determination of Arsenic in Insecticides

Application of Ion Exchange

JUNE T. ODENCRANTZ AND WILLIAM RIEMAN III

Rutgers University, New Brunswick, N. J.

METHODS are proposed for the determination of total, trivalent, and quinquevalent arsenic in insecticides. The distinctive feature of these methods is the separation of all interfering cations from the arsenic, by passage through a column of hydrogen-ion exchanger. The arsenic in the eluate is then determined by conventional iodometric procedures.

The official procedure of the Association of Official Agricultural Chemists for the determination of total arsenic in insecticides (*1*) involves reduction of arsenic to the trivalent state, separation of arsenious chloride, and iodometric titration of a neutralized and buffered aliquot of the distillate. The lengthy distillation of this procedure can be eliminated by using ion exchange to isolate the arsenic. There are other applications of ion exchange to analytical chemistry (*2*, *3*).

The proposed method for total arsenic involves oxidation of the arsenic to the quinquevalent state, separation of arsenic from interfering cations in 5 minutes by use of an ion-exchange column, and titration of the quinquevalent arsenic with thiosulfate. This procedure requires less time and space than the distillation procedure, especially when several samples are analyzed simultaneously.

REAGENTS

Hydrochloric acid, 2.0 N, 2.4 N, 6.0 N, and 12.0 N.
Nitric acid, 15.0 N.
Potassium bromate, 2.0 N.
Sodium bicarbonate, reagent grade.
Potassium iodide, reagent grade.
Standard thiosulfate solution, 0.05 N, standardized against potassium dichromate.
Sodium hydroxide, 10 N.
Phenolphthalein indicator, 1%.
Standard iodine solution, 0.05 N, standardized against arsenic trioxide.

APPARATUS

The apparatus consisted of several borosilicate glass Allihn filter tubes, 10 cm. in height and 2.7 cm. in diameter, which may be purchased from the Ace Glass Company, Catalog No. 8571 porosity B. The rate of flow through each tube was regulated by a Hoffman clamp attached to a piece of rubber tubing fitted to the lower end of the filter tube. A two-hole stopper with a 125-ml. separatory funnel was fitted into the top of each filter tube. A bed volume of 12 ml. of 60- to 100-mesh Ion-X assured the quantitative removal of all cations by the recommended procedure. This sulfonic acid resin may be purchased from Microchemical Specialties Company, 1834 University Ave., Berkeley 3, Calif.

It is necessary to regenerate the resin bed before each run. The columns are first backwashed for a few minutes by a reverse flow of water. Then 350 ml. of 2 N hydrochloric acid and 200 ml. of water are passed through each column at the rate of 20 ml. per minute.

PROCEDURES

Determination of Total Arsenic. Weigh 200 mg. of sample into a 150-ml. beaker, add 7 ml. of 15 N nitric acid, and bring to a boil on a hot plate. Add 3 ml. of 2 N potassium bromate and evaporate to dryness. Backwash and regenerate the resin during this evaporation. Dissolve the residue in 2 ml. of 6 N hydrochloric acid without heating, and add 8 ml. of water. Filter this into the separatory funnel and wash the filter with three succes-

Table I. Results of Analyses

Sample No.	Chief Metallic Constituents	A.O.A.C. Method Total As, %	Proposed Method Total As, %	Proposed Method As (III), %	Proposed Method As (V), %
1	Lead	20.96 ±0.02	20.82 ±0.04	0.00	21.07 ±0.03
2	Calcium	10.67 ±0.01	10.62 ±0.03	0.00	10.84 ±0.02
3	Calcium Copper	13.43 ±0.03	13.47 ±0.01	0.00	13.63 ±0.04
4	Copper	42.71 ±0.03	42.90 ±0.07	42.26 ±0.01	0.57 ±0.04
5	Calcium Copper	11.14 ±0.10	11.17 ±0.04	0.00	11.23 ±0.02
6	Magnesium Lead	14.47 ±0.07	14.45 ±0.07	0.00	14.81 ±0.05

sive 10-ml. portions of water. If the residue dissolves completely in the 2 ml. of 6 *N* hydrochloric acid, omit the filtration and dilute the solution to 40 ml. in the separatory funnel. Let the solution flow through the column of resin at a rate of 20 ml. per minute, and collect the eluate in a 250-ml. Erlenmeyer flask. Wash the separatory funnel and column with one 20-ml. portion and one 40-ml. portion of water.

Add 50 ml. of concentrated hydrochloric acid to the eluate to bring the concentration of this acid up to 4 *M*. Add 1 gram of sodium bicarbonate, 0.2 gram at a time, swirling all the while. Add 1 gram of potassium iodide, stopper the flask, and swirl until all the iodide is dissolved. After 5 minutes, titrate, without starch indicator, with 0.05 *N* sodium thiosulfate to the disappearance of the iodine.

Recognition of the end point may be facilitated by performing the titration on a porcelain stand. In the presence of starch, the reaction between iodine and thiosulfate is retarded, so that an appreciable quantity of thiosulfate reacts with the acid. The size of the sample should be decreased to about 0.1 gram with insecticides containing over 30% of arsenic because the end point becomes indistinct if more than 30 ml. of thiosulfate are used in the titration.

Procedure for Quinquevalent Arsenic. Weigh 200 mg. of sample into a 150-ml. beaker and add 10 ml. of 2.4 *N* hydrochloric acid. Place in a water bath between 60° and 80° for 15 minutes. Filter the sample and proceed as previously described.

Procedure for Trivalent Arsenic. Weigh 200 mg. of sample into a 150-ml. beaker and add 10 ml. of 2.4 *N* hydrochloric acid. Place in a water bath between 60° and 80° for 15 minutes. Filter the sample and wash through the column as previously described. Neutralize the acid present in the eluate with 10 *N* sodium hydroxide and adjust to the acid side of phenolphthalein with dilute hydrochloric acid. Add 4 or 5 grams of sodium bicarbonate. Titrate the solution with 0.05 *N* iodine using starch as an indicator.

RESULTS

The results of the analyses together with the mean deviations, presented in Table I, indicate that the accuracy and precision of the recommended methods are satisfactory. Each entry in the table is the mean of at least three determinations.

ACKNOWLEDGMENT

The authors are grateful to the Research Council of Rutgers University for financial aid in the investigation and to Kenneth Helrich of the Agricultural Experiment Station of Rutgers University for samples used in the analyses.

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RECEIVED October 28, 1949. Presented before the Division of Analytical and Micro Chemistry at the 116th Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J.

CRYSTALLOGRAPHIC DATA

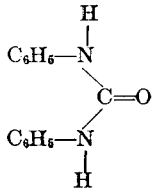
33, 34, 35. Symmetrical Diphenylurea, Unsymmetrical Diphenylurea, and Potassium Chlorate

Contributed by WALTER C. McCRONE, Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill.

IN RECENT months, inquiries have been received requesting crystallographic data on the following compounds: pentaerythritol, ether dipentaerythritol, pentaerythritol tetraformate, *o*-nitrophenol, diphenyl, apocupreine hydrobromide, and vanadium fluorides. Any information on the crystallography of these compounds, no matter how fragmentary, should be sent to the National Registry of Crystallographic Data, in care of the author, who will transmit the information to interested parties.

During the course of this program, a number of incomplete descriptions have accumulated. Although in some cases these compounds merit completion, most of them are less common or less important and would not be completed. The data are, however, accurate so far as they go and furnish adequate information for analytical purposes. Three of these partial descriptions are, therefore, being published this month. The orientations of the crystallographic axes are based on morphology and might change if x-ray diffraction data were available. Each has, however, been reoriented to agree with the conventions used in this series.

33. SYMMETRICAL DIPHENYLUREA (CARBANILIDE)



Structural Formula for Symmetrical Diphenylurea

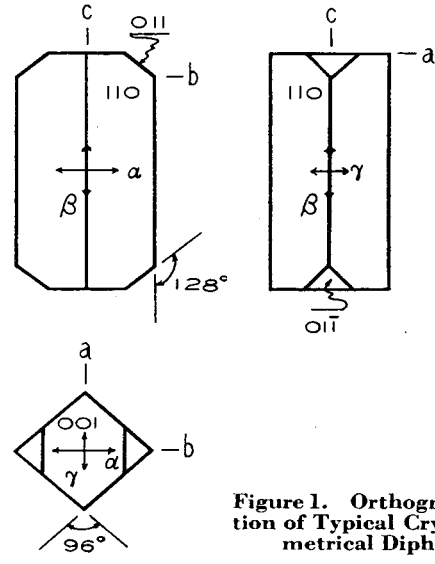


Figure 1. Orthographic Projection of Typical Crystal of Symmetrical Diphenylurea

CRYSTAL MORPHOLOGY (see Figure 1)

Crystal System. Orthorhombic.

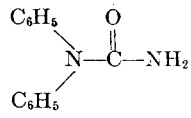
Form and Habit. Tablets from hot ethyl alcohol are flattened parallel to *b* with prism {110}, and macrodome {101}, showing also {100}, {010}, {001}, and brachydome {011}.

Axial Ratio. $a:b:c$ = 0.8957:1:0.7712; 0.8611:1:1.1165 (*3*).

Interfacial Angles (Polar). 110 ∧ $\bar{1}10$ = 96°; 011 ∧ $01\bar{1}$ = 105°.

OPTICAL PROPERTIES
Refractive Indexes (5893 A.; 25° C.). $\alpha = 1.581$; $\beta = 1.624$; $\gamma = 1.818$ (calcd.).
Optic Axial Angle (5893 A.; 25° C.). $2V = 50°$; $2E = 56°30'$ (3).
Dispersion. Strong, $r > v$.
Optic Axial Plane. 001.
Sign of Double Refraction. Positive.
Optical Orientation. $Bx_a = a$.
Density. 1.239 (3).
Formula Weight. 212.24.
Molecular Refraction. $\sqrt[3]{\alpha\beta\gamma} = 1.671$. R (calcd.) = 64.8. R (obsd.) = 64.4.

34. UNSYMMETRICAL DIPHENYLUREA



Structural Formula for Unsymmetrical Diphenylurea

Unsymmetrical diphenylurea yields good crystals from sublimation and from alcohol solutions.

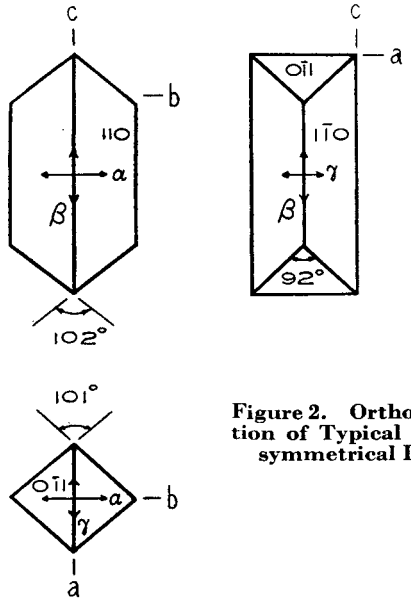


Figure 2. Orthographic Projection of Typical Crystal of Unsymmetrical Diphenylurea

CRYSTAL MORPHOLOGY (see Figure 2)
Crystal System. Orthorhombic.
Form and Habit. Tablets from hot ethyl alcohol showing the prism {110}, brachydome {011}, {010}, and {013}. The 011 faces are often replaced by a 001 face at the ends of the crystal. Generally the ideal habit is altered by the development of a 010 face upon which the crystals lie.
Axial Ratio. $a:b:c = 0.8183:1:0.8093$; $0.9891:1:1.2221$ (2).
Interfacial Angles (Polar). $110 \wedge 1\bar{1}0 = 79°$; $011 \wedge 0\bar{1}1 = 78°$.
Density. 1.276 (2).
OPTICAL PROPERTIES
Refractive Indexes (5893 A.; 25° C.). $\alpha = 1.645$; $\beta = 1.651$; $\gamma = 1.703$.
Optic Axial Angle (5893 A.; 25° C.). $2V = 38°$; $2E = 43°32'$ (2).
Dispersion. Strong, $v > r$.
Optic Axial Plane. 001.
Sign of Double Refraction. Positive.
Optical Orientation. $Bx_a = a$.
Density. 1.276 (2).
Formula Weight. 212.24.
Molecular Refraction. $\sqrt[3]{\alpha\beta\gamma} = 1.666$. R(obsd.) = 63.3 R (calcd.) = 64.0.
FUSION DATA. Unsymmetrical diphenylurea sublimes on heating to give first-order gray plates and tablets, which are usually shaded more heavily on two ends. The crystals show 90° profile angles and a Bx_0 interference figure. On further heating, melting occurs (186° C.) with very little decomposition. The melt solidifies spontaneously to give the same crystal form and orientation as is obtained on sublimation. The crystal-front is angular with all angles 90°. The crystals show parallel extinction with a slow component parallel to the direction of growth. All the crystals show a Bx_0 interference figure. When the preparation is overheated, a solid decomposition product is formed which crystallizes from the melt as high birefringent rods and needles having a positive sign of elongation.

35. POTASSIUM CHLORATE, $KClO_3$

Excellent crystals of potassium chlorate are obtained from aqueous solutions on a microscope slide.

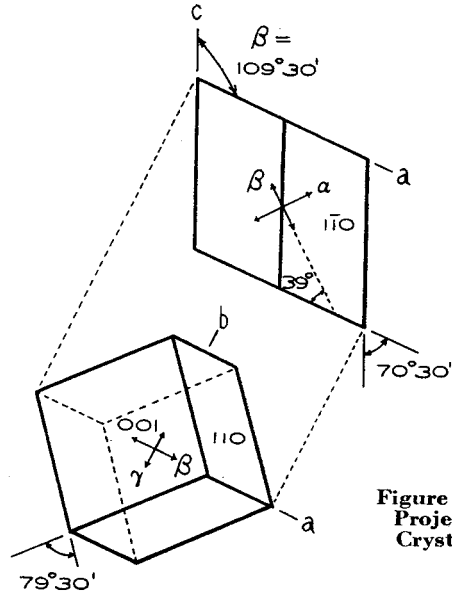


Figure 3. Orthographic Projection of Typical Crystal of Potassium Chlorate

CRYSTAL MORPHOLOGY (see Figure 3)
Crystal System. Monoclinic.
Form and Habit. Plates with clinodome, {011}; and pinacoid, {100}.
Axial Ratio. $a:b:c = 1.268:1:0.832$ (4).
Interfacial Angles (Polar). $011 \wedge 0\bar{1}1 = 76°10'$.
Beta Angle. 109°38' (4).
Twinning Plane. Parallel to 100.
X-RAY DIFFRACTION (4)
Space Group. C_{2h}^2 ($P2_1/M$).
Cell Dimensions. $a = 7.085$ A.; $b = 5.585$ A.; $c = 4.647$ A.
Formula Weights per Cell. 2.
Formula Weight. 122.55.
Density. 2.32 (1); 2.33 (x-ray).
OPTICAL PROPERTIES
Refractive Indexes (5893 A.; 25° C.). $\alpha = 1.415 \pm 0.005$ (calcd.); $\beta = 1.517 \pm 0.002$; $\gamma = 1.523 \pm 0.002$; $\beta' = 1.473$ (shown by plates lying on 001).
Refractive Index (Average). $\sqrt[3]{\alpha\beta\gamma} = 1.484$ (obsd.); 1.478 (calcd. from Gladstone's formula).
Optic Axial Angles (5893 A.; 25° C.). $2V = 28°$; $2E = 43°$.
Dispersion. Weak horizontal, $v > r$.
Optic Axial Plane. $\perp 010$.
Sign of Double Refraction. Negative.
Extinction. $a \wedge \beta = 39°$ in acute β.
Optical Orientation. $\gamma = b$; $\alpha = Bx_a$ and 58.5° from a in the obtuse angle β.

It is a pleasure to acknowledge the assistance of John Krc, Jr., in preparing this material for publication.

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CONTRIBUTIONS of crystallographic data for this section should be sent to Walter C. McCrone, Analytical Section, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Ill.

Book Reviews

Introduction to Semimicro Qualitative Chemical Analysis. *Louis J. Curtman.* Revised ed. xvi + 391 pages. Macmillan Co., 60 Fifth Ave., New York 11, N. Y., 1950. Price, $3.50.

The first edition of this text appeared in 1942 and has been successfully used in many colleges. It is conventional in its approach, one third of the book being devoted to general theoretical discussions, one fifth to the general behavior of cations and anions, and most of the remainder to experiments and to the systematic examination of unknowns.

The theoretical principles are simply but adequately explained, problems are given with answers (as they should be), and the laboratory procedures are the result of careful experiments that have stood the test of practical use. The author has used organic reagents very sparingly, and this is commendable.

A possible criticism may be voiced by those who are already using the former edition of this text—namely, that the changes and additions in the new edition are so few in number that one might wonder if a new edition is really justified. The first 188 pages are virtually without changes and the remainder of the book contains only 14 pages more than in the case of the previous edition. Of these, six are additions to the appendix. Four pages have been inserted to cover the familiar ferric chloride method for the removal of phosphate, which the author offers to those who do not wish to use his less conventional zirconyl chloride method. The remaining four additional pages represent auxiliary tests for sulfite and fluoride and a few other additions to procedures and footnotes, mostly in the anion analysis.

Briefly, therefore, this edition is a comparatively minor revision of an excellent elementary text. S. G. Simpson

Analytical Absorption Spectroscopy. Absorptimetry and Colorimetry. *M. G. Mellon,* editor. vii + 618 pages. John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y., 1950. Price, $9.

In the preface the editor states that the authors' aim was to present the material "from the viewpoint of what seems of most practical concern in a modern chemical testing and analytical laboratory." The editor and his eight contributors (L. J. Brady, W. B. Fortune, K. S. Gibson, E. R. Holiday, D. B. Judd, M. L. Moss, R. H. Müller, and E. I. Stearns) accomplish their object in nine well written chapters. Starting with an examination of the chemical requirements for the preparation of samples and of the physical principles involved in analytical absorptimetry, the book proceeds to give discussions of theory and applications and descriptions of a great variety of instruments suitable or required for work in the visible, ultraviolet, and infrared regions.

Analytical chemists will find this volume a valuable addition to their library of reference books. They will appreciate the extensive literature references, particularly of Chapter 1, which refer to the analysis of many inorganic and organic constituents. Chapter 7, "Applications of Ultraviolet and Visual Spectrophotometric Data," is also noteworthy because of the stress placed on illustrating by means of examples the many types of analytical problems that occur in a testing laboratory.

Chapter 9, "Measurement and Specification of Color," covers a vast amount of ground and apparently presupposes some knowledge of the field of color analysis. Beginners will have some difficulty with the chapter, but the citations to the relevant literature will permit those who seek more background concerning this type of testing to obtain readily the necessary information. There is some overlapping in the various chapters, but this does not detract from the value of the book. The small amount of repetition can even be considered beneficial, because it highlights factors of importance to accurate analysis. Jacob Cholak

First International Congress of Microchemistry, Graz, Austria

PHILIP W. WEST, *Louisiana State University, Baton Rouge, La.*

OVER 600 chemists met in Graz, Austria, for the First International Microchemical Congress. The meeting, which was held July 2 to 6, 1950, attracted microchemists from twenty-one countries for a program consisting of 121 lectures on pure and applied microchemistry. Those attending the congress found a wide variety of subjects covered in the program, including a number of excellent reviews which served to give an orientation on current progress. There were also exhibits of books and apparatus which attracted much attention. Although the apparatus shown was from European manufacturers only, there was a good variety displayed, and a number of demonstrations were made showing new techniques and new operational features of instruments.

The influence of Pregl and Emich on the scientific activity of Austria was obvious upon noting the large number of microchemists registered from Austria. Certainly, visitors were impressed by the tours through the laboratories of these pioneers in the field of microchemistry, and it was encouraging to see the continuing activity of the Austrian school of microchemists. One of the highlights of the Congress was the unveiling of a bust of Friedrich Emich at the opening ceremony by his daughter, Mrs. Kindler, now of Berlin. The bust was contributed by microchemists from various parts of the world and will now take its place in Graz along with that of Pregl, which had been unveiled earlier. The ceremony marked the 20th anniversary of the death of Pregl and the 10th anniversary of Emich's death.

In addition to the formal program of papers, there were a number of separate activities, such as the meetings of the Committee on New Reagents and Reactions of the International Congress of Pure and Applied Chemistry. The committee considered plans to bring out an English edition of the "Fourth Report on Reagents for Qualitative Analysis," as well as to extend its activities to include certain phases of colorimetry. A general assembly of the Congress was also held and plans were discussed for a proposed future microchemical congress to be held in 1954. Paris, Delft, Brussels, or Milan were considered as possible sites for the next meeting.

On the lighter side, the congress will be remembered for the pleasant surroundings and careful planning that made the visit in Graz such an enjoyable one. Buffets were placed near the lecture halls and many profitable sessions were held, with men from different laboratories comparing notes.

Papers presented at the congress are to be published as a regular number of *Mikrochemie vereinigt mit Mikrochimica Acta* which is scheduled to appear in September. Separate copies of this number will be obtainable at a cost of approximately $4.00; the address is Springer-Verlag, Vienna, Austria.

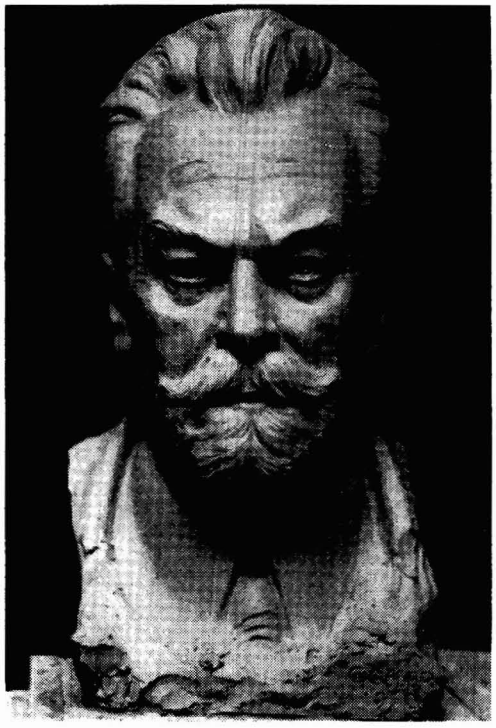
Application of Organic Complex Formers for the Separation and Determination of Metals with the Aid of Immiscible Solvents. E. Abrahamczik, Ludwigshafen on Rhein, Germany.

Standardization of Microchemical Apparatus with Special

Consideration of the Work Carried out in the U.S.A. H. K. ALBER, Philadelphia, Pa.

A Photometer for Three-Color Analysis. A. G. DE ALMEIDA, Lisbon, Portugal.

Sensitivity Limits of Optical Methods of Measurement in Microelectrophoresis and Microdiffusion. H. J. ANTWEILER, Bonn, Germany.



Bust of Friedrich Emich Unveiled at Meeting

LIST OF PAPERS PRESENTED

Iodine in Mineral Waters. Its Determination and Concentration. H. BALLEZO AND G. MONDL, Vienna, Austria.

Oxidimetric Titrations in Alkaline Solutions with Copper-3-periodate. Determination of Calcium with Naphthyl Hydroxamate. G. BECK, Bern, Switzerland.

The Scandium-Specific Groups of Pyrophosphoric Acid. G. BECK, Bern, Switzerland.

Determination of Carbon and Hydrogen in Fluorine-Containing Organic Compounds. R. BELCHER AND R. GOULDEN, Birmingham, England.

Appreciation of the Development of Micromethods. A. A. BENEDETTI-PICHLER, New York, N. Y.

A Practical and Theoretical View of Micro Hardness Testing. E. B. BERGSMAN, Vasteras, Sweden.

Microchemical Investigations on the Topical Distribution of Trace Elements in the Brain. H. BERTHA, Graz, Austria.

Method of Microdetermination of Alkali Metals Applicable to Media of Biological Origin. G. BERTRAND AND D. BERTRAND, Paris, France.

Microvolumetric Determination of Higher Titanium Contents, Especially in the Presence of Niobium. F. BISCHOFF, Graz, Austria.

New Microtechnique for the Analysis of Liquids by Displacement Adsorption. G. BLOHM, Tomteboda, Sweden.

Fossil Coloring Matters and Hydrocarbons in Limestone. N. BLUMER, Basel, Switzerland.

Molecular Weight Determination under the Microscope. M. BRANDSTATTER, Innsbruck, Austria.

Methods of Preliminary Concentration in the Spectrochemical Determination of Trace Elements. F. BURRIEL-MARTI, Madrid, Spain.

Applications of Microchemistry to Exploratory Industrial Research. N. D. CHERONIS, Chicago, Ill.

Investigations in Sedimetric Analysis. N. CHOMSE, Berlin, Germany.

Determination of Aminosalicylic Acid in Urine by Bromination. D. COPPINI AND E. COSTA, Modena, Italy.

Separation and Quantitative Determination of Small Amounts of Gases by Chromatography. E. CREMER, Innsbruck, Austria.

Behavior of Acridine Dyes as Fluoro Colors. F. DANGL, Vienna, Austria.

Micromethod for the Quantitative Analysis of Archeological Bronzes by Spectrographic Methods. M. VAN DOORSELAER, Ghent, Belgium.

Thermal Curves of Precipitates Described in the Book of Hecht and Donau. C. DUVAL, Paris, France.

Quantitative Microanalysis of "Goldoleosolen." L. EBERT AND A. DIRSCHERL, Vienna, Austria.

Development, Present State, and Outlook of Spot Test Analysis. F. FEIGL, Rio de Janeiro, Brazil, AND P. H. WEST, Baton Rouge, La.

Microdetermination of Critical Mixing Temperatures. R. FISCHER, Graz, Austria.

Living Cells as Micro Reagents. B. FLASCHENTRÄGER, Alexandria, Egypt.

Micro-Reductor Buret. H. FLASCHKA, Graz, Austria.

Semimicrodetermination of Glycolic Acid Liberated in the Course of Oxidations with Periodic Acid. P. FLEURY, J. COURTOIS, AND R. PERLES, Paris, France.

A Method of Determining Tyrothrycin with the Aid of Hemolysis. W. FRIEDRICH, Kundl, Austria.

Microdetermination of Halogens, Sulfur, and Selenium by Spectrographic Methods. A. GATTERER, Vatican.

Method of Control of the Purity of Certain Organic Compounds. M. H. GAULT, M. DORGANS, AND A. M. AZIÈRES, Paris, France.

A Complex Borotartrate and Its Application to the Research and Microchemical Determination of the Borate Ion. J. A. GAUTIER AND P. PIGNARD, Paris, France.

Photometric Determination of Small Amounts of Uranium with Potassium Thiocyanate. M. GERHOLD, Klagenfurt, Austria.

Observation of Living Chloroplasts with the Fluorescence Microscope. J. GICKELHORN, Vienna, Austria.

A Calorimetric Micromethod for the Quantitative Determination of Fusel Alcohols. S. GIERER AND O. HOFFMANN-OSTENHOF, Vienna, Austria.

Graphic Representation of the Sensitivity of Reactions. The Sensitivity Diagram. J. GILLIS, Ghent, Belgium.

Foundation of Applied Microchemistry. G. GORGACH, Graz, Austria.

Quantitative Micro-Determination of Amino Acids in Protein. G. GORBACH, Graz, Austria.

Microchemical Concentration Procedures in Emission Spectral Analysis. G. GORBACH AND F. POHL, Graz, Austria.

o-Phenanthroline as a Reagent for the Quantitative Determination of Vanadium. A. GOTTLIEB, Graz, Austria.

Search for Traces of Rare Elements with the Help of Luminescence Analysis. H. HABERLANDT, Vienna, Austria.

Colorimetric Determination of Small Amounts of Nitrate and Nitrite in Protein-Containing Substances. H. HANNI, Liebefield, Switzerland.

Micromethods for the Determination of Germanium. F. HECHT, Vienna, Austria.

The Quantitative Microanalysis of Minerals and Its Significance to Mineralogy and Geology. F. HECHT, Vienna, Austria.

Determination of Small Percentages in Iron Works Laboratories. TH. HECZKO, Linz, Austria.

New Micro Melting Point Apparatus. H. HILBCK, Cologne, Germany.

Developments in Microchemical Balance Design. G. F. HODSMAN, London, England.

Colorimetric Determination of Traces of Copper by Cuproine. J. HOSTE, Ghent, Belgium.

A New Micromethod for Molecular Weight Determination of Difficultly Volatile Substances. H. HOYER, Leverkusen, Germany.

Fluorochrome Coloring in Living Protoplasts. K. HOFLER, Vienna, Austria.

Rapid Micro Combustion Methods for the Determination of Elements in Organic Compounds. G. INGRAM, Maidenhead, England.

The Mercury Thiele Tube for the Determination of Fusion Points and for Cryoscopy. E. KAHANE, Paris, France.

(Subject not known.) E. KAHANE, Paris, France.

A Contribution in the Realm of Quantitative Organic Microanalysis. W. KIRSTEN, Uppsala, Sweden.

Fluorescence Microscope Investigation of Woody Cell Walls. J. KISSER, Vienna, Austria.

Hydrates under the Hot-Stage Microscope. A. KOFLER, Innsbruck, Austria.

Microscopic Methods in Microchemistry. L. KOFLER, Innsbruck, Austria.

Selective Oxygen Determination in Small Amounts of Gases. K. KORDESCH AND A. MARKO, Vienna, Austria.

Microchemical Training for Young People Destined for a Career in Chemistry. J. A. KUCK, New York, N. Y.

Realizations in Teaching and Research in the Realm of Microchemistry at the University of Brussels. New Chromatographic Techniques for Inorganic Separations. The Chromatographic Separation on Paper of Cations with Organic Solvents. A. LACOURT, Brussels, Belgium.

Determination of Lactic Acid. K. LANG, Mainz, Germany.

Microiodometry through Time Measurement. R. LANG, Waiblingen, Germany.

Oxidimetric Microtitration for Nitrate. W. LEITHE, Linz, Austria.

Rapid Microdetermination of Halogens in Organic Compounds. R. LEVY, Paris, France.

Lithium Aluminum Hydride as a Reagent for Microanalytical Determination of Functional Groups. H. LIEB AND W. SCHÖNIGER, Graz, Austria.

Cobalt Detection. A. D. LLACER AND J. A. SOZZI, Buenos Aires, Argentina.

Microchemistry in Practical Pharmacy. F. LÜDY-TENGER, Burgdorf, Switzerland.

Limits of Absorption Spectral Analysis. A. LUSZCZAK, Vienna, Austria.

The Separation of Metal-Organic Complexes. A. K. AL MAHDI AND C. L. WILSON, Belfast, Ireland.

Application of Kofler's Micromethod in Plant Microchemistry. D. MARKOVIĆ, Zagreb, Jugoslavia.

Proposed Improvements for the Rapid Selective Determination of Organic (or Mineral) Halogens by Chemical Methods. F. MARTIN, Vitry, France.

Rapid Microdetermination of Sulfuric Ash in Organic Matter (Determination of Alkali Metals). F. MARTIN, Vitry, France.

Kjeldahl Microdetermination of Cyclic Nitrogen. M. MARZADRO, Rome, Italy.

Contribution on the Determination of Trace Elements in Minerals. ST. MIHOLIĆ, Zagreb, Jugoslavia.

Application of *o*-Dianisidine as Redox Indicator in Microanalysis. G. MILAZZO AND L. PAOLONI, Rome, Italy.

The Spectrographic Determination of Trace Elements in Rocks, Minerals, and Soils. R. L. MITCHELL, Aberdeen, Scotland.

Microhardness and Type of Binding. R. MITSCHE AND E. M. ONITSCH, Leoben, Austria.

Determination of Knyurenic and Xanthurenic Acids. L. MUSAJO AND D. COPPINI, Modena, Italy.

Twenty-five years of Teaching Quantitative Organic Microanalysis at New York University. J. B. NIEDERL, New York, N. Y.

Topological Microanalysis by the Use of X-Rays. M. PAIĆ, Zagreb, Jugoslavia.

Micro Melting Point Determination in Forensic Chemistry. W. PAULUS, Bonn, Germany.

A Colorimetric Method for the Determination of Oxalic Acid. R. S. PEREIRA, São Paulo, Brazil.

Spectrographic Determination of Traces of Nickel and Cobalt by Extraction with Ferrous Sulfate. R. PIERUCCINI, Florence, Italy.

Colorimetric Determination of Small Amounts of Manganese with Arnold's Reagent. W. PRODINGER, Vienna, Austria.

The Microdetermination of Amido and α-Amino Nitrogen by the Method of Concentrated Hydrochloric and Nitric Acids. M. RENARD AND P. DESCHAMPS, Liége, Belgium.

Analysis of Sugar Mixtures by Colorimetric Method. H. RÜGGEBERG, Detmold, Germany.

Microdetermination of Iodine Number. W. RUZICZKA, Vienna, Austria.

Ion Adsorption on Paper and Glass Surfaces. T. SCHÖNFELD AND E. BRODA, Vienna, Austria.

Microcolorimetric Procedure for the Determination of Small Amounts of Gold in Ores. H. SCHREINER, Graz, Austria.

New Titrimetric Methods in Gas Analysis. Iodometric Determination of Oxygen in Gas Mixtures. Iodometric Determination of Nitrous Oxide. E. SCHULEK, Budapest, Hungary.

Narcosis and Stimulation of Protoplasm. W. SEIFRITZ, Philadelphia, Pa.

Catalyzed Iodine-Azide Reaction in Microanalysis. I and II. P. SENISE, São Paulo, Brazil.

Filament Chromatography. G. SKALOS, Athens, Greece.

Micromethods for the Determination of Physical Constants. M. SOBOTKA, Graz, Austria.

New Chromatographic Separation of Mixtures of Iron, Aluminum, and Titanium on the Microgram Scale. GH. SOMMEREYNS, Brussels, Belgium.

Microchemical Methods Applied to Industrial Materials. C. E. SPOONER, Manchester, England.

Semimicrodetermination of Some Constituents of Milk by Chromatographic Separation. J. STERNBERG, J. COLAS, AND T. KAHN, Paris, France.

Colorimetric Determination of Picric Acid in Picrates of Organic Bases. R. STÖHR AND F. SCHEIBL, Innsbruck, Austria.

Interesting Examples of Applied Microanalysis. R. STREBINGER, Vienna, Austria.

Microchemistry in Gas Liquor Research. K. STUNDL, Graz, Austria.

Microchemistry in the Service of Iron Works and Steel Mill Chemists. C. SWOBODA, Kapfenberg, Austria.

Elementary Analytical Determination of Oxygen, a Carbon-Hydrogen Determination Developed from It, and a New Method of Carrying Out the Dumas Nitrogen Determination for Difficultly Combustible Substances. J. UNTERZAUCHER, Leverkusen, Germany.

Recent Progress in the Sensitivity of Optical Methods for the Identification and Determination of Organic Substances. Applications to Biochemical Microanalysis. M. VACHER, Paris, France.

Experience in the Microdetermination of Mercury and Lead in Biological Material. R. VESTERBERG, Tomteboda, Sweden.

Absorption of Cobalt by Pasture Grass, Studied by Means of the Radioactive Tracer Method. J. DE WAEL, Utrecht, Netherlands.

Survey of One Procedure of Organic Elementary Analysis. H. WAGNER, Vienna, Austria.

Determination of Vitamins by Microchemical Methods. H. WALDMANN, Basel, Switzerland.

The Role of Microchemistry in the New Realms of Analytical Chemistry. P. E. WENGER, Geneva, Switzerland.

Microdocimastic Determination of the Oligodynamics of Silver. R. WERNER, Düsseldorf, Germany.

The Analyst's Calendar

Group for Advancement of Spectrographic Methods

The Group for the Advancement of Spectrographic Methods, 1 Place St. Thomas d'Aquin, Paris 7, France, has planned a meeting in Strasbourg on October 12 to 14, 1950, to discuss the improvements made during the past 10 years in the spectrographic analysis of industrial products. Investigators from all countries are invited to attend and to submit papers in duplicate with a 20-line abstract before September 15. The general themes of the meeting are: drifts, direct analysis, standards, luminous sources, and analysis of metalloids and occluded gases.

Society for Applied Spectroscopy

The Society for Applied Spectroscopy has planned a meeting on September 12, which will begin with an informal dinner at 6 P.M. at Tosca's, 118 Fulton St., New York, N. Y. At 8 P.M. a business meeting will be held at the Socony-Vacuum Training Center, 63 Park Row, New York. There will be no formal speaker, but plans for the coming season will be outlined by the new officers and committees.

Electron Microscope Society of America. Hotel Statler, Detroit, Mich., September 14 to 16. Eighth annual meeting

Instrument Conference and Exhibit. Instrument Society of America, Buffalo, N. Y., September 18 to 22

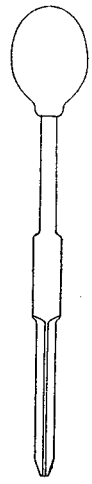
Optical Society of America. Cleveland, Ohio, October 26 to 28

Fourth Symposium on Analytical Chemistry. Louisiana State University, Baton Rouge, La., January 29 to February 1, 1951

AIDS FOR THE ANALYST.....

Extraction Pipet for Spot Test Analysis. Jack K. Carlton, Louisiana State University, Baton Rouge, La.

IN ORDER to apply extraction techniques to spot test analysis and preserve the essence of the spot test method, a small and simple device was needed, in which the component liquids could be thoroughly mixed and allowed to separate as rapidly as possible. A dropper pipet, with a few modifications, satisfied these requirements.



The pipet consists of a capillary tip 6 cm. long, 7 mm. in outside diameter, and 1.8 mm. in inside diameter; a bulb blown just above the capillary tip, 4 cm. long, 1.15 cm. in outside diameter, and about 2- to 3-ml. capacity; an upper stem 5 cm. long, 7 mm. in outside diameter, and 5 mm. in inside diameter; and a rubber bulb of 10-ml. capacity. The over-all length of the pipet is approximately 15 cm. None of these dimensions is critical. When low boiling liquids such as ether, chloroform, carbon tetrachloride, and carbon disulfide are used as extractants, a capillary of about 0.7- or 0.8-mm. bore is recommended.

Mixing is accomplished by drawing the liquids into the pipet and then expelling them, repeating the procedure several times, quickly. By using a rubber bulb of considerably greater capacity than that of the pipet, a large quantity of air is drawn into the pipet after the liquids have been drawn up, and the bubbling of this air through the two liquid layers provides a very efficient mixing of the two layers.

Care should be exercised in using the pipet to avoid the loss of the liquids being mixed. When the liquids are drawn into the pipet the pressure of the fingers on the rubber bulb should be released slowly, so that when the air begins to bubble through, the liquids will not spatter into the rubber bulb or on the sides of the upper stem, to which droplets might adhere and consequently be lost. On expulsion, pressure should be applied to the rubber bulb slowly to avoid spattering when the air begins to bubble through the liquids which have been passed into a small beaker.

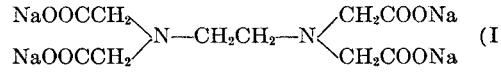
The use of extraction techniques in spot test analysis offers a means of separating an ion from its interferences which might prove valuable in a manner similar to the use of masking agents. West and Carlton [(ANAL. CHEM., 22, 1055 (1950))] use such an extraction in separating gold from the platinum metals. For such work the extraction pipet described should find useful application.

The author wishes to express his appreciation for financial assistance given him under a contract with the Office of Naval Research.

Cleaning Sintered-Glass Filtration Crucibles. W. M. Budde and S. J. Potempa, Loyola University, Chicago, Ill.

IN MANY cases the collection of inorganic precipitates on sintered-glass crucibles is more convenient than using filter paper or asbestos mats. However, sintered-glass crucibles tend to become clogged after a certain amount of use, and in many cases the precipitate is difficult to remove—for example, barium sulfate.

The present work has shown that the tetrasodium salt of ethylenediamine tetraacetic acid (I) (available under the trade name Versene at low cost from the Bersworth Chemical Company, Framingham, Mass.) will very readily dissolve many precipitates encountered in gravimetric work.

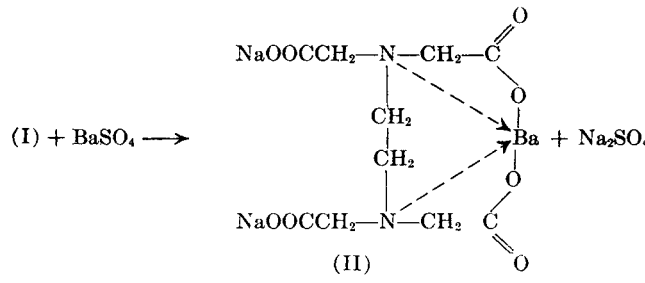


(I)

A hot 0.1 molar solution of the dry salt was found to be effective in dissolving the precipitates listed below. (A reliable private source has indicated that this material will dissolve practically any insoluble metallic compound, except sulfides and ferricyanides.)

Aluminum oxide
Barium sulfate
Calcium oxalate
Calcium phosphate
Cupric hydroxide
Lead carbonate
Lead iodate
Lead oxalate
Magnesium ammonium phosphate
Magnesium carbonate
Magnesium sulfate

It is generally thought that the substance dissolves precipitates [Schwarzenbach and Ackermann, *Helv. Chem. Acta*, **31**, 1029 (1948)] by a complex formation (II), as shown for barium sulfate.



(II)

Even thoroughly dried precipitates can be easily removed from the pores of sintered-glass filtration crucibles when a hot 0.1 molar solution of the tetrasodium salt of ethylenediamine tetraacetic acid is drawn through the funnel by means of suction, or when the clogged crucible is placed in a vessel filled with a hot 0.1 molar solution. In most cases the sintered-glass plate is completely freed of precipitate in a matter of seconds.

A definite advantage of this method over using hot acids is that the tetrasodium salt is almost completely nontoxic, does not cause burns if brought into contact with the skin, is inexpensive, and can be used as a water-softening agent for general laboratory cleaning.

Sintered-glass crucibles which have been used to filter permanganate solutions soon accumulate a film of difficultly removable manganese dioxide. This can be removed by pouring cold dilute solutions of sodium bisulfite and sulfuric acid alternately through the crucible while gentle suction is applied. This method works better on a fresh precipitate than on one that has been allowed to dry.